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1. On the Colour and Polarization of the Light scattered by Sulphur Suspensions.

By Bidhubhusan Ray, M Sc, Lecturer in Optics, Calcutta University

I HISTORICAL INTRODUCTION

The problem of the scattering of light by small suspended particles has attracted a great deal of attention in view of its bearing on the explanation of the blue colour of the sky and of the sea. Some of the earliest experiments on the subject were those made by Tyndall who attempted to explain the polarization and colour of the sky, as due to the scattering of light by very small particles in suspension in the higher atmosphere. He imitated the blue light of the sky in his laboratory by having a cloud of very small particles in a tube, containing Iodide of allyl. The fine particles were formed by the action of light on the liquid.

The late Lord Rayleigh¹ next took up the problem and studied the scattering of light by suspensions of sulphur obtained by adding a drop or two of very dilute sulphuric acid to a weak solution of sodium hyposulphite. At first the scattered light seen in a perpendicular direction is completely polarized, but as the particles began to grow in size, the light is not extinguished in any position of the Nicol but in the position of minimum illumination shows Tyndall's phenomena of the "Residual Blue," proving that for the shortest waves, the polarization of the scattered light is relatively more imperfect. The direction of maximum polarization now becomes oblique and moves back towards the source. Prof Love² next treated the problem mathematically limiting himself

¹ Scientific Papers, Vol I and Vol IV.

² Lond Math Soc Proc. Vol 30, p. 308.

to the case of spherical particles but without any limitations as to their refractive indices and (so far as the general expressions are concerned) to their radii as well. Owing to the omission of some factors in his equations, some discrepancies arose. The late Lord Rayleigh corrected the results and put them in a very simple form. These equations will be referred to again later on.

Bromwich¹ has given a general solution of the problem of the scattering when a plane simple harmonic electromagnetic wave strikes a sphere. In certain cases a marked simplification is introduced by using spherical polar co-ordinates. When certain assumptions are imposed upon the particles as regards their size and nature, the equations obtained by Bromwich are identical with those obtained by the late Lord Rayleigh, though expressed in a different form. In the case of large perfectly conducting spheres, the formulæ given by Bromwich have been utilised by Messrs Proudman, Doodson and Kennedy² who have made numerical calculations for the case of $ka=9$ and 10 , where $k=\frac{2\pi}{\lambda}$ and a =radius of the spherical particles. Here they found that the curve showing the variation of the intensity of the light scattered in different directions is of an oscillatory character.

In course of a study of the phenomena of the "Residual Blue" in the light scattered by sulphur suspensions obtained by Rayleigh's method, the author was induced to continue his observations to a stage at which the particles had grown much larger in size, and found that oscillations of the intensity of the light scattered in different directions were readily observable. They were somewhat similar to those shown in the curves published in the paper by Messrs Proudman, Doodson and Kennedy, but the characters of the curves for the light polarized in and right angles to the plane of scattering in this case were found to be interchanged. The difference is not surprising, as in the present instance we are dealing with sulphur particles which are not at all perfectly conducting spheres. It is proposed first to give a general description of the author's observations and then to discuss the results on the basis of the rigorous electromagnetic theory of diffraction.

¹ Phil Trans Series A, Vol. 220, 1920.

² Phil. Trans. Series A, Vol. 217, 1917.

2 EXPERIMENTAL RESULTS.

The experimental arrangements required are of the simplest kind. Light from an 1,000 c.p. lamp is focussed by a lens upon a rectangular slit behind which was placed a beaker of clear water, 15 to 20 drops of a very weak solution of sodium thiosulphate is added to the water in the beaker and 4 to 5 drops of very dilute sulphuric acid are then put in and the liquid stirred. A fine precipitate of sulphur slowly forms which scatters the light passing through the liquid. Care should be taken not to add more acid than absolutely necessary as the formation of sulphur particles is then unduly hastened and the phenomena now to be described cannot be satisfactorily observed. The best results are obtained when the quantity of acid is just sufficient to cause the first blue colour to appear after 15 minutes.

As the sulphur suspension gradually forms, the colour and polarization of the light scattered by it change in a remarkable manner. For qualitative observations it is convenient to view the scattered light with the eye placed above the beaker, the illuminated portion of the liquid being as near the surface as possible. For purpose of measurement of the angles of scattering, the scattered light from the centre of the beaker may be observed through the sides of the vessel. The scattered light varies in intensity and colour in different directions and when observed through a Nicol, changes as the Nicol is rotated about its axis.

Lord Rayleigh observed that "In the early stages of precipitation, polarization is complete in a perpendicular direction and incomplete in other directions. After an interval the polarization begins to be incomplete in a perpendicular direction, the light which reaches the eye when the Nicol is in the position of minimum transmission being of beautiful blue colour, much richer than any thing that can be shown in the earlier stages." At this stage the polarisation is more complete in a direction with $\theta =$ positive, i.e. back towards the source. When the particles increase in size, a neutral point comes in near $\theta = 0$ with still further increase, this neutral point moves away towards $\theta = 180^\circ$, and between the neutral direction and $\theta = 0$, the relative intensity of the two components is interchanged, in other words, the state of polarization of the scattered light is now reversed. Lord Rayleigh observed such reversal with blue light only. The author has con-

firmed Lord Rayleigh's work and also extended his investigations to much larger particles. It is found that with larger particles this reversal can be seen with red light and it is possible to follow up the movement of the neutral direction to a stage in which it is nearly $\theta = 180^\circ$. Further with white light, the scattered light shows a succession of colours in different directions, these colours being different for the two components of polarization. The observations are tabulated below.—

TABLE I.
Colours of the Scattered Light.

Time from Commencement	Orientation of the Nicol	Description of Colour and direction of Scattered Light	REMARKS
15 min		*Blue colour (Residual blue) max being at 90°	Light scattered nearly paral to the direction of transmission is white but slightly tinged blue.
	⊥	White patch (but slightly bluish)	
30 min		Brownish red *blue $\theta = 0$ to $\theta = 60^\circ$ $\theta = 60^\circ$ to $\theta = 135^\circ$	Transmitted light is yellowish white
	⊥	slightly brownish tint $\theta = 0$ to $\theta = 85^\circ$	
45 min		Brownish red colour disappears and greenish blue appears extending from $\theta = 0$ to $\theta = 120^\circ$,, ,
	⊥	Blue Brownish red $\theta = 0$ to $\theta = 85^\circ$ $\theta = 85^\circ$ to $\theta = 135^\circ$	
1 hr		Greenish yellow from $\theta = 0$ to $\theta = 110^\circ$ other colours cannot be distinguished	,, ,
	⊥	Brownish red *green $\theta = 0$ to $\theta = 70^\circ$ $\theta = 70^\circ$ to $\theta = 112^\circ$ Red $\theta = 112^\circ$ to 140°	

|| component is the component having its vibrations in the plane containing the direction of the incident ray and the direction of observation. The vibration is perpendicular to the direction of observation.

⊥ is the component having its vibrations perpendicular to the above plane. The vibration is also perpendicular to the direction of observation.

* Indicates that the colour is very pronounced.

TABLE II.

Colours of the Scattered Light

Time from Commencement	Orientation of the Nicol	Description of Colour and direction of Scattered Light			
1 hr 12 min.		Brown $\theta=0$ to $\theta=65^\circ$	Green $\theta=65^\circ$ to $\theta=110^\circ$	The transmitted light turns a bit reddish.	
	\perp	Bluish green: $\theta=0$ to $\theta=60^\circ$	Crimson red: $\theta=60^\circ$ to 110° Rosy red, $\theta=130^\circ$ to 180°	*Greenish yellow $\theta=100^\circ$ to 130° the colour being pronounced at $\theta=160^\circ$	
1 hr 22 min		Yellowish green $\theta=0$ to $\theta=65^\circ$	Light brown $\theta=65^\circ$ to 97°	Greenish white $\theta=97^\circ$ to 120° Transmitted light is reddish	
	\perp	Light red $\theta=0^\circ$ to 60°	*Greenish yellow $\theta=60^\circ$ to 85°	*Orange red $\theta=85^\circ$ to 114°	Yellow $\theta=114^\circ$ to 140° Red light till $\theta=180^\circ$, colour most pronounced at 160°
1 hr 35 min		Greyish green $\theta=0$ to $\theta=88^\circ$	Brown red $\theta=88^\circ$ to 117°	Green $\theta=117^\circ$ to 140°	Transmitted light is red
	\perp	Light red $\theta=0$ to $\theta=55^\circ$	Yellow $\theta=55^\circ$ to 92°	Orange red $\theta=92$ to 117°	Yellow $\theta=117^\circ$ to 135° Transmitted light is red, colour most pronounced at $\theta=165^\circ$

|| component is the component having its vibrations in the plane containing the direction of the incident ray and the direction of observation. The vibration is perpendicular to the direction of observation

\perp is the component having its vibrations perpendicular to the above plane. The vibration is also perpendicular to the direction of observation

* Indicates that the colour is very pronounced

A few observations were made of the direction of the maxima in the scattered light in this case using red and yellow glasses respectively to approximately monochromatize light. The following results are tabulated for the case in which the Nicol is in the \perp position. The observations clearly indicate that the colours of the scattered light arise mainly from the fact that the directions of the maxima and the minima are different for different wave lengths

	Angle θ — Position of the Maximum		
Red	45°	105°	165°
Yellow		75°	125°

3 THEORETICAL

Let us suppose that a beam of unpolarized light falls on a spherical obstacle with its centre as the origin and also let the light travel in the negative direction along the axis of Z . Suppose we confine our observation to the horizontal plane (i.e. plane containing Z, X) at a distance r from the centre and making an angle θ with incident beam. We can observe both the horizontal and the vertical components of the scattered light with the help of a Nicol at the point in question.

If X, Y and Z denote the electric forces parallel to the three axes in the scattered wave then the vertical component of the scattered light is denoted by Y while the horizontal one by

$$\frac{xZ - zX}{r}.$$

Love's solution as corrected and modified by the late Lord Rayleigh gives the following expressions for the two components.

$$Y = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} \left[M_n (\mu P_n' - n(n+1) P_n) + N_n P_n' \right] \frac{e^{ik(ct-r)}}{kr}$$

$$xZ - zX = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} \left[N_n (\mu P_n' - n(n+1) P_n) + M_n P_n' \right] \frac{e^{ik(ct-r)}}{kr}$$

In these equations, $k = \frac{2\pi}{\lambda}$, λ being the wave length of the incident light, $\mu = \cos \theta$ and P_n or $P_n(\mu)$ is a zonal harmonic of degree n , whose axis is the axis of Z . Mod Y and Mod $\frac{xZ - zX}{r}$ give the amplitudes of the two components and their squares give the intensities. M_n and N_n are functions of the size and optical proportions of the spherical particles. The complete expression for

N_n is

$$K\psi_{n-1}(\eta) - \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} \right\} \psi_n(\eta)$$

$$K - E_{n-1}(\eta) + \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} \right\} E_n(\eta)$$

and
 M_+

$$\frac{\psi_{n-1}(\eta) - \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} \psi_n(\eta)}{-E_{n-1}(\eta) + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} E_n(\eta)}$$

The expression for M_+ is obtained by substituting μ the magnetic permeability, instead of K . In optical problems we may take $\mu=1$ so the expression for M_+ stands as above.

K is the dielectric constant of the material composing the spherical particle, that of the surrounding medium being supposed equal to unity. K may be substituted for m^2 where m is the refractive index of the material composing the sphere, relatively to the surrounding medium, and $\eta^2 = m \cdot \eta$.

$$\psi_n = (-1)^n \cdot 1 \cdot 3 \cdot 5 \cdot 7 \cdot 9 \cdots (2n+1) \left(\frac{1}{\eta} \frac{d}{d\eta} \right)^n \frac{e^{in\eta}}{\eta}$$

and

$$\overline{E_n} = (-1)^n \cdot 1 \cdot 3 \cdot 5 \cdot 7 \cdot 9 \cdots (2n+1) \left(\frac{1}{\eta} \frac{d}{d\eta} \right)^n \frac{e^{-in\eta}}{\eta}$$

so that

$$E_n(\eta) = \psi_n(\eta) - i \overline{\psi_n}(\eta)$$

when real and imaginary parts are separated.

4 CALCULATIONS WITH SULPHUR PARTICLES.

The late Lord Rayleigh in the same paper calculated the values of Mod Y and Mod $\frac{xZ - iX}{r}$ for various values of η , not greater than 2.25 assuming $K=2.25$ (an arbitrary value). He also suggested that "It would be possible to follow these calculations to greater values of η , and such an extension would not be without interest, but the arithmetical work would soon become heavy. Also, without increasing η , the refractive index might be varied." It was thought that in the case of sulphur the equations given above would explain the oscillations of the colours of the scattered light in different directions if numerical calculations were made with the appropriate data. As these colour fluctuations were observed when the particles were larger than those responsible for the Tyndall's "Residual blue" phenomenon, it was only reasonable that calculations should be made for larger values of η or (ka) where

a —radius of the particle. Refractive index for sulphur particles is 1.95 and that of water 1.33. K was accordingly taken to $\left(\frac{1.95}{1.33}\right)^2$ and the numerical values were computed on the assumption that $Ka=5$.

In order to calculate the values of $E_n(\eta)$, the sequence formula was used

$$E_{n+1} = \frac{(2n+1)(2n+3)}{\eta^2} [E_n - E_{n-1}]$$

starting from E_0 and E_1 . This method is satisfactory as regards the real part of $E_n(\eta)$, but as the imaginary part tends to equality, any error, then may creep in, is multiplied at the next step by the large factor $(2n+1)(2n+3)$. The difficulty can be overcome in the following manner when the convergence is good. We may calculate the value of ψ_0 and ψ_{10} by a straight forward method very accurately. Having obtained them we may then use the sequence formula in a reverse direction to find the lower values of ψ_n without any loss of accuracy.

The values of ψ and χ were calculated for $\eta=5$ and tabulated below

Tables of ψ and χ

	ψ	χ
0	056748	— 19175
1	— 108264	— 05704
2	— 099009	080827
3	01295	19302
4	28214	28273
5	1 066	35524
6	4 484	41478
7	26 664	46443
8	226 236	506412
9	2578.44	5424

Tables for M_n and N_n .

	M_n	N_n
1	— 4978— 1×4529	— 5555— 1×7061
2	— 1713— 1×0030	— 2881— 1×0913
3	— 2423— 1×0626	— 3926— 1×8098

	M_n	N_n
4	— 3453— $1 \times .8616$	0287— $1 \times .9992$
5	.4998— $1 \times .5131$.4812— $1 \times .3642$
6	0554— $1 \times .0031$	1476— $1 \times .0223$
7	.00475— $1 \times .00002$	0124— $1 \times .0015$
8	00036— 1×0	0013— 1×0
9	00002— 1×0	0001— 1×0

The quantities,

$$\left\{ \frac{2n+1}{n(n+1)} \mu P'_n - (2n+1) P_n \right\} \text{ or } A_n \text{ and } \frac{2n+1}{n(n+1)} P'_n \text{ or } B_n$$

are functions of n and η . Their logarithmic values for various values of μ have been tabulated by Rayleigh¹ up till $n=6$ and their actual numerical values have been given by Paris² for $n=5$. Calculations have been pushed up to $n=9$ yet the tables are not given as the values A_n , M_n , B_n , M_n , etc., decrease rapidly

Table for Mod Y and Mod $\frac{xZ-zX}{r}$

	$\left(\text{Mod } \frac{xZ-zX}{r} \right)$	$(\text{Mod } Y)^2$
1	11 88	11 88
.95	8 12	2 15
.75	79	6 76
.6	2 1	9 12
.5	3.54	11 91
.4	8.23	14 26
.25	13 71	4 52
0	5.46	14 01
— 25	9.15	21 25
— .4	14.8	11 32
— .5	19.01	5.54
— .75	42 18	17 44
— 95	110 72	127.79
— 1	376 57	376.57

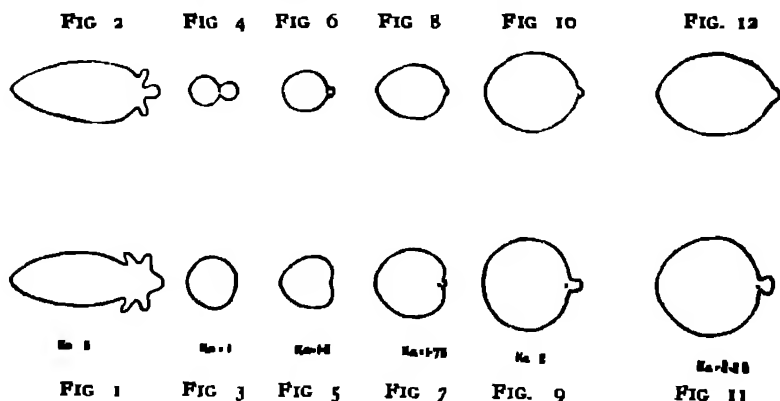
Polar diagrams have been drawn (Figs. 1 and 2) representing (intensity)¹ or Mod Y and Mod $\frac{xZ-zX}{r}$. The form of the graphs shows the remarkable resemblance between the theoretical and

¹ Royal Soc. Proc Ser A, Vol. 84

² Phil. Mag Vol 30, 1915.

observed phenomena. It shows that the \perp component of the scattered light shows 3 oscillations while the \parallel one shows only 2. It also shows that the max and min. of Fig 1 (\perp Component) are sharper and steeper than those of Fig. 2 (\parallel Component). This also is the actual case, where the number of oscillations is greater in the \perp component than the \parallel one; the colours in the former component are more prominent.

The graphs drawn in Figs 1 and 2 evidently correspond more or less closely to the stage after 1 hr and 35 minutes in Table II.



Also from the graph in Figs 1 and 2 it is seen that the maxima are more pronounced when θ approaches 180° . This is in agreement with observation as the intensity of the colour increases in that direction. In order to get a clear idea of how the light scattering alters with the size of the particles for the two states of polarization, the numerical data given by the late Lord Rayleigh¹ for $ka=1$, $ka=1.5$, $ka=1.75$, $ka=2$ and $ka=2.25$ have been plotted as polar diagrams in Figs 3 to 12. It will be noticed that the \parallel component which has no intensity when $\theta=90^\circ$ and ka is small shows fewer and less marked fluctuations with increasing values of ka . The tendency is clear even when $ka=1.75$ and becomes patent for still larger values of ka .

The radius of the particles in Table II and after 1 hr. 30 min from commencement was found to range between 0.3μ to 0.5μ being thus of the same order of magnitude as that indicated by the character of the light scattered by them.

¹ Proc Roy Soc. Ser A, Vol. 84, 1911

5. SUMMARY AND CONCLUSION

1 The colour and polarization of the light scattered in different directions by very fine suspensions of sulphur have been studied by the late Lord Rayleigh. In the present paper, the work is extended to much larger particles and some very remarkable results have been obtained. It is found that for the larger particles the curves representing the intensity of the light scattered in different directions become of an oscillatory character, the phenomena being markedly different for light having its electric vector \parallel and \perp to the plane of scattering containing the incident and scattered rays.

2 Rayleigh observed that at the early stages, as the particles increase in size the position of maximum polarization shifts towards the source. With still further increase in the size of the particles, a neutral direction appears nearly at $\theta=0$ which gradually begins to shift towards $\theta=180^\circ$. Between the neutral direction and $\theta=0^\circ$, the state of the polarization of the scattered light is reversed. Rayleigh observed such reversion only with blue light. The author has pushed the investigation to larger particles and observed such reversal with red light and traced further the movement of the position of the neutral direction to about $\theta=180^\circ$.

3 In the earlier stages, as the particles form, it is found that the \parallel component shows more pronounced fluctuations of intensity and colour, than the \perp component, the latter showing hardly any trace of variation of intensity with direction. As the particles increase in size, the position is reversed (see Tables I and II of the paper). The \perp component now shows a larger number of oscillations, and the colours in it are more prominent than those of the \parallel component. The colour sequence alters in the manners indicated in Tables I and II. The intensity curves are somewhat like those published by Messrs Proudman, Doodson and Kennedy¹ for perfectly conducting particles except that the characters of the curves for \parallel and \perp component are here interchanged. The difference is due to the fact that in this case we are dealing with particles of sulphur which are transparent, and not with perfectly reflecting particles.

¹ Phil Trans Vol. 217, 1917

4 In order to explain the phenomena, the theoretical formulæ have been numerically computed for the case in which $ka=5$ and the results are found to agree with the observed facts.

5 The colours of the transmitted light as seen by Porte and Keen¹ will be theoretically discussed in a separate paper.

The investigation here described was carried out in the Palit Laboratory at the University College of Science and the author is indebted to Prof C. V Raman, Palit Professor of Physics, for the unfailing interest he has taken during the progress of the work

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The 5th May, 1921

¹ Roy Soc Proc Vol 89, Ser A

II. On the Vibrations of the Pianoforte-String.

By Panchanon Das, M.Sc , Research Scholar in the Indian Association for the Cultivation of Science.

The main features of the vibrations of the pianoforte-string were first elucidated by Helmholtz, who assumed the force exerted by the hammer during impact to be of the form $F \sin pt$. Next, Kaufmann¹ discussed it on different lines with the aid of functional solutions of the equation of wave-motion, but his treatment in the most important case, viz that of a string struck not far from one end, was only approximate. Prof C. V Raman² and B. Banerji, worked out the problem in a more complete manner by regarding the motion during impact as that of a loaded string and by taking into account the discontinuous changes in the pressure of the hammer due to the successive reflections of the impulse from the ends of the string. Kaufmann's work can also be extended so as to give more accurate results by working out the successive functional solutions. This method is not so cumbersome as might be apprehended, in fact the results are very simple and elegant in form

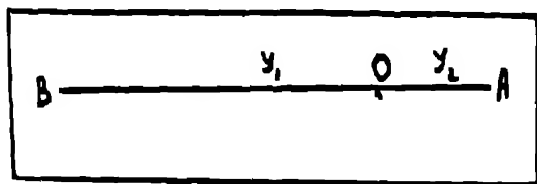


FIG. 1.

Fig 1, represents a pianoforte-string. O is the position of the point where the hammer strikes the string and A is the fixed end of the same, the length OA being equal to a . We assume that the length a is so small, or rather the other end of the string

¹ Annalender Physik Band 54 (1895). ² Proc Royal Society A, Vol 97 (1920).

attached to the bridge B is so remote from O , that the impact ceases before the wave reflected from the bridge-end reaches O . For the present we restrict ourselves to the case of a rigid hammer for the simplicity of its treatment, the case of an elastic hammer will be discussed later on. The following are the symbols used in the paper —

- m = Mass of the hammer.
 ρ = linear density of the string.
 T = tension of the string.
 c = wave-velocity in the string
 v_0 = initial velocity of the hammer
 t = variable time.

We take the x -axis along OA , and for simplicity suppose the vibrations to be in a plane passing through OA and \perp to OA . Let the displacement at any point of the string at any instant t be y_1 for positive values of x , y_0 at O and y_1 for negative values of x .

We divide the duration of the impact into a series of epochs determined by $0 < ct < 2a$, $2a < ct < 4a$, $4a < ct < 6a$, and so on, so that each of these epochs corresponds to the time taken by a pulse from O in returning to O after reflection from the end A . It will be found, as easily follows from general considerations, that the motion of the string is different at different epochs. So it is necessary to investigate the motion in each of these succeeding epochs.

I Epoch ($0 < ct < 2a$) —

The equation of motion of the string on each side of O is

$$\frac{\partial^2 y}{\partial t^2} = c^2 \frac{\partial^2 y}{\partial x^2},$$

and that of the hammer is

$$m \frac{d^2 y_0}{dt^2} = T \left(-\frac{\partial y_1}{\partial x} + \frac{\partial y_1}{\partial x} \right)_{x=0} \dots \dots \dots (1)$$

As the hammer impinges on the string, two waves of the same form start in both directions of the string, so that the displacements are

$$\left. \begin{aligned} y_1 &= f_1(ct + x) \\ y_2 &= f_1(ct - x) \\ y_0 &= f_1(ct) \end{aligned} \right\} \dots \dots \dots (2)$$

However from after $ct=a$, a pulse corresponding to the reflection of $f_1(ct-x)$ from the end A will affect the value of y_2 , but that pulse will not reach O , until $ct=2a$, so that if we confine our attention to the immediate neighbourhood of O , the value assumed in (2) is sufficiently representative in the First Epoch.

Substituting (2) in (1) we get,

$$\text{or} \quad mc^2 f_1''(ct) + 2T f_1'(ct) = 0, \quad f_1''(ct) + k f_1'(ct) = 0, \quad \dots \dots \dots (3)$$

where
$$k = \frac{2T}{mc^2} = \frac{2\rho}{m}$$

The first integral is

$$f_1'(ct) = C e^{-kct}$$

When $t=0$, $y_0 = v = c f_1'(c) = cC$

$$C = \frac{V_0}{c}$$

Thus,
$$f_1'(ct) = \frac{V_0}{c} e^{-kct} \quad \dots \dots \dots (4)$$

II. Epoch ($2a < ct < 4a$) .—

The wave $y_2 = f_1(ct-x)$ of the first epoch is reflected back as a wave $-f_1(ct+x-2a)$, and reaches O at $ct=2a$. This is easily seen from the fact, that $f_1(ct-x) - f_1(ct+x-2a)$ produces a node at $x=a$. We shall suppose that this reflected wave is transmitted unaltered through O , but excites fresh waves in the positive and negative directions of the x -axis, while the original wave f_1 continues. To satisfy the condition of continuity of displacement at O , these two waves, thus supposed to be excited, must be of the same functional form, i.e. $f_2(ct-x)$ and $f_2(ct+x)$ respectively. We then write

$$\left. \begin{aligned} y_1 &= f_1(ct+x) + f_2(ct+x) - f_1(ct+x-2a) \\ y_2 &= f_1(ct-x) + f_2(ct-x) - f_1(ct+x-2a) \\ y_0 &= f_1(ct) + f_2(ct) - f_1(ct-2a) \end{aligned} \right\} \dots \dots \dots (5)$$

Substituting these in (1) and simplifying the results with the help of (3), we get

$$f_2''(ct) + k f_2'(ct) = f_1''(ct-2a) \dots \dots \dots (6)$$

Writing x for ct , we get the first integral,

$$\begin{aligned} f_2'(x) e^{kx} &= C_2 + \int f_1''(x-2a) e^{kx} dx \\ &= C_2 + f_1'(x-2a) dx - k \int f_1'(x-2a) e^{kx} dx. \end{aligned}$$

Substituting from (4) we get

$$f_2'(z)e^{kz} = C_2' + \frac{V_0}{c}e^{2ak} - \frac{V_0K}{c}e^{2ak}(z-2a)$$

Or,
$$f_2'(z) = C_2'e^{-kz} + \frac{V_0}{c}e^{-k(z-2a)} \left\{ 1 - k(z-2a) \right\}.$$

At $ct=2a$, the value of y_0 calculated from the I Epoch equals that calculated from the II Epoch

Thus,
$$f_1'(2a) + f_2'(2a) - f_1'(0) = f_1'(2a)$$

or
$$f_2(2a) = f_1'(0) = \frac{V_0}{c} \quad \dots \dots \dots (7)$$

Hence
$$C_2' = 0, \quad \dots \dots \dots (7a)$$

$$f_2'(ct) = \frac{V_0}{c}e^{-k(ct-2a)} \left\{ 1 - k(ct-2a) \right\} \quad \dots \dots \dots (8)$$

III. Epoch ($4a < ct < 6a$) —

We now proceed to apply the same method to the third and subsequent epochs. The pulse $f_2(ct-x)$ is reflected from the end A as $-f_2(ct+x-2a)$ and this after incidence on the hammer gives rise to two new pulses $f_3(ct-x)$ and $f_4(ct+x)$ along OA and OB respectively. The pulses f_1 and f_2 and their reflections still continue. Thus, the displacements are

$$\begin{aligned} y_1 &= f_1(ct+x) + f_2(ct+x) + f_3(ct+x) \\ &\quad - f_1(ct+x-2a) - f_2(ct+x-2a) \\ y_2 &= f_1(ct-x) + f_3(ct-x) + f_4(ct-x) \\ &\quad - f_1(ct+x-2a) - f_2(ct+x-2a) \\ y_0 &= f_1(ct) + f_2(ct) + f_3(ct) \\ &\quad - f_1(ct-2a) - f_2(ct-2a) \end{aligned} \quad (9)$$

Substituting these in (1) and simplifying the result from (3) and (6) we get

$$f_3''(ct) + kf_3'(ct) = f_3''(ct-2a) \quad \dots \dots \dots (10)$$

The first integral is

$$\begin{aligned} f_3'(z)e^{kz} &= C_3 + e^{kz}f_2'(z-2a) - k \int e^{kz}f_2'(z-2a)dz \\ &= C_3' + \frac{V_0}{c}e^{4ak} \left\{ 1 - k(z-4a) \right\} \\ &\quad - \frac{V_0K}{c}e^{4ak} \left\{ (z-4a) - k \frac{(z-4a)^2}{2} \right\}. \end{aligned}$$

Equating again the values of y_0 from the II and III Epochs at $ct=4a$, we get

$$f_3'(4a) = f_2'(2a) = \frac{V_0}{c}$$

$$C_3' = 0 \quad \dots \quad (10a)$$

Hence,

$$f_3'(ct) = \frac{V_0}{c} e^{-k(ct-4a)} \left\{ 1 - 2k(ct-4a) + \frac{k^2}{2}(ct-4a)^2 \right\} \quad (11)$$

IV Epoch ($6a < ct < 8a$) --

Exactly similar arguments show that, a new pulse $f_4(z)$ is called into play.

The equation of motion reduces to

$$f_4''(z) + kf_4'(z) = f_3''(z-2a) \quad \dots \quad (12)$$

Integrating, we get

$$f_4'(z)e^{kz} = C_4' + \frac{V_0}{c} e^{kz} \left\{ 1 - 3k(z-6a) + \frac{3k^2}{2}(z-6a)^2 - \frac{k^3}{6}(z-6a)^3 \right\} \dots (13)$$

Again, from the continuity of velocity at $ct=6a$ at 0, we get

$$f_4'(6a) = f_3'(4a) = \frac{V_0}{c} \quad \dots$$

$$C_4' = 0 \quad \dots \quad (13a)$$

Hence,

$$f_4'(ct) = \frac{V_0}{c} e^{-k(ct-6a)} \left\{ 1 - 3k(ct-6a) + \frac{3k^2}{2}(ct-6a)^2 - \frac{k^3}{6}(ct-6a)^3 \right\} \dots (14)$$

Generalisation --

It will thus be seen that the end of every epoch, say the n^{th} , a new pulse $f_{n+1}(z)$ is brought into existence, and its form is given by the differential equation

$$f_{n+1}''(z) + kf_{n+1}'(z) = f_n''(z-2a) \quad \dots \quad (15)$$

as is seen from the results (6), (10) and (12).

Also, the suitably adjusted constant of integration vanishes, as is seen from (7a), (10a) and (13a).

Thus comparing the forms of f_2' , f_3' , f_4' we deduce that corresponding to the V Epoch ($8a < ct < 10a$),

$$f_5'(z) = \frac{V_0}{c} e^{-k(z-8a)} \left\{ 1 - 4k(z-8a) + \frac{6k^2}{2}(z-8a)^2 - \frac{4k^3}{6}(z-8a)^3 + \frac{k^4}{24}(z-8a)^4 \right\}$$

Generalising the result by the method of induction we have, for the $(n+1)^{th}$ epoch, ($n.2a < ct < \overline{n+1.2a}$),

coordinates, and let x, y be the coordinates of an element of the wave-surface $P'YP$. Then if ρ be the distance of the point R from the element (x, y) , the disturbance at R due to the latter may be represented by a periodic expression of the form $\cos k(at - \rho)$ where $k = 2\pi/\lambda$. Expressing ρ in terms of the coordinates chosen.

we have

$$\begin{aligned}\rho^2 &= (x - \xi)^2 + (y - \eta)^2 \\ &= f^2 - 2x\xi - 2y\eta + \xi^2 + \eta^2, \quad f \text{ being the focal length} \\ &= f^2 - 2s\xi - 2f\eta \cos \theta + \xi^2 + \eta^2 \text{ approx}\end{aligned}$$

where s is the length of the arc measured from Y to the point (x, y) along $P'YP$, and θ the angle which that arc subtends at O . On further transformation

we get

$$\begin{aligned}\rho^2 &= (f - \eta)^2 + \xi^2 - 2s\xi + 2f\eta(1 - \cos \theta) \\ &= \rho_0^2 - 2s\xi + \frac{\eta^2}{f} \text{ since } s = f\theta = f \sin \theta \text{ approx}\end{aligned}$$

Hence

$$\rho = \rho_0 - \frac{\xi}{\rho_0} s + \frac{\eta}{2\rho_0^2} s^2 \quad (\text{approx})$$

ρ_0 being the distance of R from Y

Or we may write, substituting f for ρ_0 in the small terms,

$$\rho = \rho_0 - \frac{\xi}{f} s + \frac{\eta}{2f^2} s^2 \quad (\text{approx})$$

The total disturbance at R due to the whole wave will be given by

$$\int_{-\sigma}^{\sigma} \cos k \left(at - \rho_0 + \frac{\xi}{f} s - \frac{\eta}{2f^2} s^2 \right) ds \quad (1)$$

This will also represent the resultant magnetic intensity at R

The electric intensity at the point will have for its components

$$E_x = \int_{-\sigma}^{\sigma} \cos \phi \cos k \left(at - \rho_0 + \frac{\xi}{f} s - \frac{\eta}{2f^2} s^2 \right) ds \quad (2)$$

$$E_y = \int_{-\sigma}^{\sigma} \sin \phi \cos k \left(at - \rho_0 + \frac{\xi}{f} s - \frac{\eta}{2f^2} s^2 \right) ds. \quad (3)$$

where ϕ is the angle which the vector from the element of the wave under consideration makes with a direction parallel to OY . Since ϕ is always small, we may write approximately $\cos \phi = 1$ and

$\sin \phi = (\xi - s)/f$. The expressions then become, after some further transformations,

$$H = E_x = C_0 \cos k(at - \rho_0) + S_0 \sin k(at - \rho_0) \quad \dots (4)$$

$$E_y = C_1 \cos k(at - \rho_0) + S_1 \sin k(at - \rho_0) \quad \dots (5)$$

where

$$\begin{aligned} C_0 &= \int_{-\sigma}^{\sigma} \cos (ls - ms^2) ds \\ S_0 &= \int_{-\sigma}^{\sigma} -\sin (ls - ms^2) ds \\ C_1 &= \int_{-\sigma}^{\sigma} \frac{\xi - s}{f} \cos (ls - ms^2) ds \\ S_1 &= \int_{-\sigma}^{\sigma} -\frac{\xi - s}{f} \sin (ls - ms^2) ds \\ l &= k\xi/f \text{ and } m = k\eta/2f^2 \end{aligned} \quad (6)$$

The direction of the time-mean of the vector $[\mathbf{E}, \mathbf{H}]$ will determine the direction of the line of flow of energy at the point. Hence if ψ be the angle which the line of flow makes with the direction OY , we have

$$\tan \psi = \frac{\overline{H L_y}}{\overline{H L_x}} = \frac{C_0 C_1 + S_0 S_1}{C_0^2 + S_0^2}$$

This is the differential equation of the lines of flow. We may now put the four integrals C_0 , C_1 , S_0 and S_1 in a form suitable for calculation, expressing them in terms of Fresnel integrals or in terms of Lommel Functions. Since the addition of a constant term in the periodic part does not affect the time-mean value of the expressions for E and H , equations (4) and (5) will continue to hold if

$$\begin{aligned} C_0 &= \int_{-\sigma}^{\sigma} \cos m \left(s - \frac{l}{2m} \right)^2 ds = \int_{-\sigma}^{\sigma} \cos m \left(s - \frac{\xi}{\eta} f \right)^2 ds \\ S_0 &= \int_{-\sigma}^{\sigma} \sin m \left(s - \frac{\xi}{\eta} f \right)^2 ds \end{aligned}$$

mation be made, in the part of the field which is of most interest, i.e. near the focus, to reduce the equation to an easily integrable form. The lines have therefore to be drawn directly from the differential equation by calculating the direction of flow at successive points and tracing out the lines bit by bit. The curves in the accompanying *plate* have been drawn thus, the direction of a line being determined at successive intervals of $\frac{\pi}{10}$ in the value of $(k\xi\sigma/f)$.

There is also another expression in terms of Lommel Functions which is suitable for numerical calculation at a distance from the focus. Starting from equations (6), we have

$$C_0 = \int_{-\sigma}^{\sigma} \cos(ls - ms^2) ds = 2 \int_0^{\sigma} \cos ls \cos ms^2 ds = Z \text{ (say)} \quad (14)$$

$$S_0 = \int_{-\sigma}^{\sigma} -\sin(ls - ms^2) ds = 2 \int_0^{\sigma} \cos ls \sin ms^2 ds = 2 Z' \text{ (say)} \quad (15)$$

$$\begin{aligned} &= \int_{-\sigma}^{\sigma} \frac{\xi - s}{f} \cos(ls - ms^2) ds \\ &= \frac{2\xi}{f} Z - \frac{2}{f} \int_0^{\sigma} s \sin ls \sin ms^2 ds \\ &= \frac{2}{f} Z \left(\xi - \frac{l}{2m} \right) + \frac{1}{mf} \sin l\sigma \cos m\sigma^2 \quad \dots \quad (16) \end{aligned}$$

Similarly

$$S_1 = \frac{2}{f} Z' \left(\xi - \frac{l}{2m} \right) + \frac{1}{mf} \sin l\sigma \sin m\sigma^2 \quad \dots \quad (17)$$

so that

$$\tan \psi = \left(\frac{\xi}{f} - \frac{l}{2mf} \right) + \frac{1}{2mf} \sin l\sigma \frac{Z \cos m\sigma^2 + Z' \sin m\sigma^2}{Z^2 + Z'^2} \dots \quad (18)$$

or since $l = k\xi/f$ and $m = k\eta/2f^2$

$$\tan \psi = \frac{\xi}{f} - \frac{\xi}{\eta} + \frac{f}{k\eta} \sin l\sigma \frac{Z \cos m\sigma^2 + Z' \sin m\sigma^2}{Z^2 + Z'^2} \dots \quad (19)$$

We may now proceed to express Z, Z' in terms of Bessel's functions.

$$Z = \int_0^{\sigma} \cos ls \cos ms^2 ds = \int_0^{\sigma} \left(\frac{\pi ls}{2}\right)^{\frac{1}{2}} J_{-\frac{1}{2}}(ls) \cos ms^2 ds$$

$$= \left(\frac{\pi}{4m}\right)^{\frac{1}{2}} \left\{ U_{\frac{1}{2}} \cos m\sigma^2 + U_{3/2} \sin m\sigma^2 \right\} \quad (20)$$

where $U_{\frac{1}{2}}, U_{3/2}$ are Lommel functions defined by

$$U_n = \sum_{s=0}^{\infty} (-1)^s \left(\frac{2m\sigma}{l}\right)^{n+2s} J_{n+2s} \quad \dots \quad (21)$$

Similarly

$$Z' = \left(\frac{\pi}{4m}\right)^{\frac{1}{2}} \left\{ U_{\frac{1}{2}} \sin m\sigma^2 - U_{3/2} \cos m\sigma^2 \right\} \quad \dots \quad (22)$$

Hence

$$\tan \psi = \frac{\xi}{f} - \frac{\xi}{\eta} + \frac{f}{k\eta} \sqrt{\frac{4m}{\pi}} \sin l\sigma \frac{U_{\frac{1}{2}}}{U_{\frac{1}{2}} + U_{3/2}}$$

$$= \frac{\xi}{f} - \frac{\xi}{\eta} + \frac{\xi}{\eta} \sin x \cdot \frac{P_1 \sin x + Q_1 \cos x}{(P_1 \sin x + Q_1 \cos x)^2 + (P_2 \sin x + Q_2 \cos x)^2}$$

where $x = k\xi\sigma/f$

$$P_1 = 1 - a^2 \left(\frac{3}{x^4} - 1 \right) + a^4 \left(\frac{105}{x^4} - \frac{45}{x^2} + 1 \right) -$$

$$Q_1 = a^4 \frac{3}{x} - a^4 \left(\frac{105}{x^3} - \frac{10}{x} \right) +$$

$$P_2 = \frac{a}{x} - a^3 \left(\frac{15}{x^3} - \frac{6}{x} \right) + a^5 (\quad) -$$

$$Q_2 = -a + a^3 \left(\frac{15}{x^2} - 1 \right) - a^5 (\quad)$$

$$a \text{ being written for } \left(\frac{\eta}{\xi} \frac{\sigma}{f} \right).$$

The expressions are obtained by expanding the Lommel functions in a series of Bessel functions and then substituting semi-convergent expansions for the latter (see Gray and Mathews, Bessel Function, p. 42). The expansions are useful as the terms converge rapidly in regions well outside the geometric cone, a being then small.

Some principal features of the lines of flow as drawn from the above calculations may now be noted. The first thing that strikes us is the remarkable concentration of the lines when approaching the focus. Most of the lines of flow originating

within the geometrical cone of light (represented by the dotted lines in the Plate) from the aperture crinkle down to the central maximum in the focal plane, a fact which is but to be expected in view of the large concentration of light that is known both experimentally and from the elementary theory of diffraction to occur at the focus. Secondly, the lines of flow which reach down to a point at a distance from the focus originate near the boundary of the aperture, and this perhaps explains the luminosity of the boundary of the aperture when viewed from behind a small obstacle covering the focus. The lines of flow are practically straight lines radiating to the focus, except in the close neighbourhood of the focus itself where the crinkling is much more pronounced. The "visibility" of the fringes observed in any plane depends on the amplitude of the crinkles, and hence increases as the plane of observation is moved down towards the focal plane and the Fresnel class is gradually transformed to the Fraunhofer class of diffraction phenomena.

IV. On some Indian Stringed Instruments.

Physics in the Calcutta University

(Plate I)

CONTENTS

- I —Introduction
 II —The Form of the Bridge in the "Taupura" and the "Vina"
 III —The Failure of the Young Helmholtz Law
 IV —Outline of Mechanical Theory
 V —Summary

I. INTRODUCTION

study of the numerous kinds of musical instruments to be found in
doubted antiquity and disclose a remarkable appreciation of acoustic principles. An investigation of their special features, in comparison with those of instruments of other countries may be expected to yield results of great interest. An instance of the fruitfulness of the line of work here suggested is to be found in the present author's research on the Indian Musical Drum, which have been found to embody in a practical form the solution of the problem of loading a circular drumhead in such a manner as to
as a stringed instrument.¹ In the present paper it is proposed to offer a preliminary note on the results of the author's study of

2 THE FORM OF THE BRIDGE IN THE "TANPURA" AND THE "VINA"

The "Tanpura" and the "Vina" are two of the most highly valued indigenous stringed instruments intended to be excited by plucking. Plate I, Fig 1 illustrates the form of the "Tanpura". This instrument has no frets and is intended merely to be used as a drone in accompaniment with vocal or other music. It has four metal "strings" which are stretched over a large resonant body and can be accurately tuned up to the right pitch by a simple device for continuous adjustment of tension. The remarkable feature of the "Tanpura" to which I wish to draw attention is the special form of bridge fixed to the resonant body over which the strings pass. The strings do not come clear off the edge of a sharp bridge as in European stringed instruments, but pass over a curved wooden surface fixed to the body which forms the bridge. The exact length of the string which actually touches the upper



FIG 3 —The Bridge of the Tanpura

surface of the bridge is adjusted by slipping in a woollen or silken thread of suitable thickness between each string and the bridge below it and adjusting its position by trial. Generally the thread is moved forwards or backwards to such a position that the metal "string" just grazes the surface of the bridge. The description will be clearer on a reference to Fig 3 above where the bridge and the string passing over it are indicated diagrammatically.

The "Vina" on the other hand is a fretted instrument intended for use in playing melodies (Fig 2 in Plate I). The form of the bridge adopted in it differs from that of the "Tanpura" in two respects. The upper curved surface of the bridge in the "Vina" is of metal, and the special mode of adjustment of contact by means of a thread used in the "Tanpura" is dispensed with, and the string merely comes off the curved upper surface of the bridge at a tangent, as indicated diagrammatically in Fig. 4.



Fig 1 Tanpura



Fig 2 Vina

(No attempt is made in this figure to indicate the exact form of the lower part of the bridge.)



FIG 4 --The Bridge of the Vina

The bridge of the "Vina" is also much higher above the body of the instrument than in the "Tanpura." Even when the strings are pressed down on the frets when the instrument is being played, the curvature of the upper surface of the bridge ensures the string always leaving the bridge at a tangent to it as shown

3 THE FAILURE OF THE YOUNG-HELMHOLTZ LAW

The special form of bridge illustrated above has a very remarkable influence on the tone-quality. This can be most readily demonstrated in the "Tanpura." When the adjustment of contact of string and bridge is made carefully by trial, the instrument is highly sonorous, giving a tone of fine musical quality. If on the other hand the grazing contact of string and bridge is rendered inoperative (as for instance by inserting a small piece of metal between the string and the surface of the bridge)" the tone becomes dull and insipid. A similar remark applies also to the case of the "Vina," though the difference is less striking in the latter case

In attempting to find an explanation for the difference in tone-quality produced by the special form of bridge, the author made a surprising observation, namely, that in the tone of the "Tanpura" or the "Vina," overtones may be heard powerfully which according to known acoustical principles should have been entirely absent. According to the law enunciated by Young and Helmholtz, if the string is plucked at a point of aliquot division, the harmonics having a node at the point of excitation should be entirely absent. This law may be readily verified on an ordinary sonometer with the usual form of bridge. For this purpose, the position of the node should first be found exactly by trial by putting the finger in contact with the string and plucking else-

where so as to elicit the overtones desired. Having found the position of the node, the string should be plucked exactly at that point and then again touched with the finger *at the same point*. On an ordinary sonometer, this results in the sound being immediately quenched inasmuch as the finger damps out all the partials except those having a node at the point touched, and the latter are not excited in the first instance in accordance with the Young-Helmholtz law. On trying the same experiment with the "Vina" or the "Tanpura", it will be found that the overtone having a node at the plucked point sings out powerfully. In fact the position of the plucked point hardly appears to make a difference in regard to the intensity of the overtones in the "Tanpura". This remarkable result is not due to any indefiniteness in the position of the node point, as the latter is found to be quite well defined as is shown by the fact that in order to demonstrate the effect successfully, the string must be plucked and then touched exactly at that right point otherwise the sound is quenched. We are thus forced to the conclusion that the effect of the special form of bridge is completely to set aside the validity of the Young-Helmholtz law and actually to manufacture a powerful sequence of overtones including those which ought not to have been elicited according to that law.

4. OUTLINE OF A MECHANICAL THEORY

Some photographs of the vibration-curves of a "Tanpura" string were made at the suggestion of the author by Mr Ahmed Shah Bukhari at the Government College, Lahore, last November. They showed that in consequence of the grazing contact at the bridge, the vibration of the string decreased in amplitude and altered its form at a much more rapid rate than when the grazing contact was rendered ineffective. A more complete investigation is obviously desirable. From first principles, however, it is obvious that in the 'Tanpura' the forces exerted by the vibrating string on the bridge must be very different from what they would be for a bridge of ordinary form. It seems probable that by far the greater portion of the communication of energy to the bridge occurs at or near the point of grazing contact. The forces exerted by the string on the bridge near this point are probably in the nature of impulses occurring once in each vibration of the string.

This would explain the powerful retinue of overtones including even those absent initially in the vibration of the string. At a slightly later stage, the reaction of the bridge on the string would result in a modification of the vibration form of the latter and bring into existence partials absent initially in it. There would in fact be a continual transformation of the energy of vibration of the fundamental vibration into the overtones.

The foregoing explanation of the character of the tones of the "Tanpura" would not be fully applicable to the "Vina" as the forces exerted by the string on the bridge in this case would not be purely of an impulsive character. There is however a certain portion of the bridge over which the string comes into intermittent contact during the vibration, and it seems very probable that the theory for this case is intermediate in character between that for the 'Tanpura' and those for stringed instruments with bridges of the ordinary type. Further experimental work is needed in support of this view.

5 SUMMARY

The present paper deals with the remarkable acoustic properties of the "Tanpura" and the "Vina" which are two of the most highly reputed among Indian stringed instruments. The form of the bridge used in these instruments is quite different from that usually found in European stringed instruments. In the 'Tanpura' the string passes over the wooden upper surface of the bridge which is curved to shape, and by insertion of a thread of wool or silk, a finely adjustable grazing contact of string and bridge is secured. In the 'Vina' the upper surface of the bridge is of curved metal and the string leaves it at a tangent. The tones of these instruments show a remarkable, powerful series of overtones which gives them a bright and pleasing quality. Experiment with these instruments shows that the validity of the Young-Helmholtz law according to which partials having a node at the plucked point should not be excited is completely set aside. A possible mechanical explanation of this result is suggested.

V. Note on the Omori-Ewing Seismograph.

By Dr Gilbert T Walker, C.S.I Sc D , F.R.S.

[Extract from a letter to Prof C V Raman with reference to the preceding paper]

In connection with your very interesting stringed instrument it may be convenient to have a more definite statement regarding the apparently somewhat similar effect observable with seismographs

As you probably know in the Omori-Ewing pattern the heavy weight, which forms part of a horizontal pendulum with a period of say 40 seconds, is prevented from moving too far and perhaps breaking the instrument during a violent earthquake by stops and it has been noticed that when owing to faulty adjustment the heavy weight is in contact with one of these the amplitude of the resulting record is greatly magnified I think the explanation is fairly simple. If the ground has a harmonic motion of total amplitude $2a$ and frequency m the period being of the order of two seconds, then the maximum velocity will be am . Let us suppose that this motion occurs only for a time π/m which will be comparable with one second We suppose as the simplest possible case that the stop and the weight, being initially in equilibrium, are then in contact, and that the stop, owing to the motion of the ground, suddenly starts away from the weight with velocity am on its return to the weight it will suddenly impart to it this velocity, and the ground then is supposed to come to rest The total amplitude $2b$ of the swing of the weight will be connected with its natural frequency n by the equation $bn=am$ Thus the amplitude of the swing of the weight after being struck by the stop bears to what it would have been if the stop had not been there the ratio b/a or m/n , which is comparable with 20 Of course in practice the motion is complicated by the motion of the column from which the instrument is suspended and by subsequent motion of the ground; but as a first approximation I regard the result as correct. The motion of the weight is magnified on the trace but the ratio of the amplitudes on the trace corresponding to contact with the stop and the normal adjustment is of course still b/a .

VI. Some Observations on Interference Phenomena in Non-Homogeneous Light.

By Nihal Karan Sethi, D.Sc., Assistant Professor of Physics
in the Benares Hindu University.

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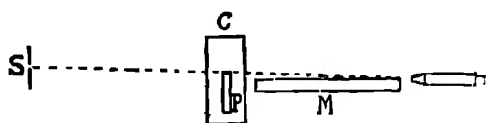
SECTION III.—Summary

SECTION I —DISPERSION OF WHITE-LIGHT FRINGES BY A RETARDING PLATE.

It is well known that when a thin plate of some transparent substance is introduced in the path of one of two interfering beams, e.g. in Lloyd's single mirror experiment, the effect is to shift the interference fringes by n fringe-widths towards the path of the beam which is retarded, where $n = (\mu - 1) \frac{D}{\lambda}$ and D is the thickness of the plate. And in the case of illumination with white light also, in spite of the dispersion of the plate, the system of fringes appears to shift as a whole without any change in their number or appearance except that as found by Airy and Stokes, the central or achromatic band shifts to a slightly greater extent than might be expected from the foregoing expression. Its achromatism also does not remain as perfect as before the introduction of the plate. The present writer has, however, found a very simple but interesting case in which the introduction of a retarding plate completely abolishes the achromatic band and what is more increases the number of fringes observable with white light to a very considerable extent. And still more surprising is the fact that any attempt at partially monochromatising

the light by interposing coloured screens in its path actually diminishes instead of increasing the number of visible fringes.

To perform the experiment, Lloyd's fringes are first obtained in the usual manner and a microscope carefully focussed on them. In front of the mirror *M* (Fig 1) which forms these fringes is placed a cell *c* containing a mixture of carbon bisulphide and benzene, the composition of which has been adjusted till its refractive index is equal to that of the glass plate for the blue end of the spectrum. The retarding plate *P* which is a plate of glass about a millimeter or two or even 5 mm in thickness is immersed in this cell in such a manner that one of the two interfering beams passes through it while the other passes through the liquid mixture only. Further, the glass plate should be on the same side as the mirror producing the fringes. When the position of this plate has been carefully adjusted by shifting the cell, a surprisingly large number of fringes will be observed in the field of view, and they will all appear to be coloured. Start-



ing from near the edge of the plate (as seen in the microscope) the brighter fringes will be found to gradually change their colour from red to orange, yellowish white, green and then blue. The darker fringes which are only slightly weaker in intensity, will be found to have a colour more or less complementary to the neighbouring brighter fringes, except in the region in the middle of the field where the colours are hardly noticeable. Seen through a red glass, the fringes towards the edge of the plate appear to gain in contrast but the rest of the fringes vanish altogether. A yellow or green glass shifts the region of maximum visibility to about the middle of the field and a blue-violet glass makes the fringes at the other end distinctly better but completely destroys those towards the edge of the plate. The width of these fringes is also not constant but decreases gradually from the red side of the field towards the blue.

The effect observed here is no doubt of the same nature as the shift of the achromatic band by a retarding plate discussed by

Airy and Stokes, differing from it in that the magnitude of the shift in the present instance differs very largely for different groups in the spectrum. It has been shown by the late Lord Rayleigh¹ that the shifted position of this band is given by the relation

$$R + \left(\mu - 1 - \lambda \frac{d\mu}{d\lambda} \right) D = 0 \quad \dots (A)$$

where D and μ are respectively the thickness and the refractive index of the plate and R is the relative retardation due to other causes. In the usual case, the introduction of the dispersion term $\lambda \frac{d\mu}{d\lambda}$ involves only a small correction, for $\mu - 1$ is relatively much larger and D cannot be increased to any great extent. In the present case, however, this relation becomes

$$R + \left\{ (\mu - \mu') - \lambda \left(\frac{d\mu}{d\lambda} - \frac{d\mu'}{d\lambda} \right) \right\} D = 0 \quad \dots (B)$$

so that the effective value of the first term within the curled brackets has been greatly reduced throughout the spectrum and would actually vanish for the wave-length for which the refractive indices of the plate and liquid are equal, while the second term depending on the difference of the dispersive powers remains finite throughout. At the same time in the present case, the value of D has been considerably increased. The result is that, while usually the regions of maximum visibility in the field for different groups in the spectrum are more or less coincident, they will not be so with the present arrangement, for equation (B) is satisfied for different wave-lengths at points in the field well separated from each other. We thus have what might be called the dispersion of the achromatic band, the groups near the red end of the spectrum showing the fringes best near the edge of the plate and the groups near the blue end relatively far out in the field. The observable fringes are thus spread out over a large extent and we have their number greatly increased.

It is evident that the visibility of the fringes measured in terms of the total intensity of illumination in the bright and dark portions must suffer very considerably in this process, for in that part of the field where, for example, the fringes are best seen

¹ Phil. Mag. Sept. 1904 and Scientific Papers, Vol. V. p

in red light, the rest of the spectrum must be producing a fairly strong and more or less uniform illumination. The colour of this uniform illumination will, however, be bluish and the visibility resulting from the contrast of colour will be quite good for we shall have in juxtaposition two such widely different colours as red and bluish green

Attention may also be drawn to the fact that the experiment described above may be very conveniently used to illustrate the fact that the shift of the region of best visibility is determined by the difference of group-velocity of light in the plate and the liquid and not by the difference of wave-velocity; for if the refractive index of the liquid mixture is adjusted to be equal to that of the glass plate for any specified part of the spectrum, say the green, we may have zero retardation for light of this colour, but the fringes are visible far out in the field and not near the edge of the plate. If, on the other hand, the refractive index of the liquid mixture is so adjusted that the group-velocity for red light is identical in the glass plate and the liquid,¹ the red fringes remain at the edge of the plate and do not shift out, although the glass has now a decidedly greater refractive index than the liquid and hence retards the waves. As the refractive index of the liquid is gradually altered, the side on which the plate should be introduced in order to enable the shifted fringes to be observed with Lloyd's mirror, does not require to be changed at the stage at which the wave-velocities in the two media are equal but as in the case of Powell's bands, at the stage when the group-velocities are identical.

It seems probable that the large increase in the number of white-light fringes in an interferometer and their breaking up into groups observed by R. W. Wood² on introducing sodium vapour into the path of one of the beams is essentially of the same nature as the phenomenon described above. In Wood's experiment, as in the present case, the term $\mu - 1$ is small and

$\lambda \frac{d\mu}{d\lambda}$ becomes relatively much larger specially in the neighbourhood of the sodium absorption band. The achromatic fringe is,

¹ See a paper by the present author on "Powell's bands and the Group-velocity of light in dispersive media," *Phy. Rev.* Dec. 1920, p. 519

² *Phil. Mag.* Sept. 1904, and Wood's *Physical Optics*, second edition, p. 141.

therefore, dispersed over a considerable part of the field and in opposite directions on the two sides of the sodium line resulting in the visible fringes breaking up into groups and in an increase of their number. The latter effect is not fully explained in Wood's paper and in the appendix to it by the late Lord Rayleigh.

A similar increase in the number of fringes should also be observed on introducing a moderately thick plane-parallel glass plate in the path of one of the interfering beams in a Michelson Interferometer, and adjusting the moveable mirror to bring back the white-light fringes. In this case much greater thickness of the glass plate can be used than in the experiment with Lloyd's fringes, and although $\lambda \frac{d\mu}{d\lambda}$ is small in comparison with $\mu - 1$ of equation (A) above, the increased thickness of the glass plate causes the separation of the different groups of waves. If t is the distance through which the moveable mirror is shifted, it is evident that the maximum visibility for a group of waves with wave-length λ will be obtained when

$$t - \left\{ (\mu - 1) - \lambda \frac{d\mu}{d\lambda} \right\} D = 0$$

If t_1 and t_2 are the values of t for red and violet groups respectively,

$$t_2 - t_1 = \left\{ (\mu_2 - \mu_1) - \left(\lambda_2 \frac{d\mu}{d\lambda_2} - \lambda_1 \frac{d\mu}{d\lambda_1} \right) \right\} D$$

And if $\mu = A + \frac{B}{\lambda^2}$,

$$t_2 - t_1 = 3 B.D \left\{ \frac{1}{\lambda_2^3} - \frac{1}{\lambda_1^3} \right\}$$

With $D = 1$ cm and $B = 5 \times 10^{-10}$, this will give $t_2 - t_1 = .003$ cm approximately. This is equivalent to

$$\frac{2 \times .003}{6 \times 10^{-5}} = 100 \text{ wave-lengths.}$$

So that in this case about a hundred fringes should be visible. It is also evident that they will exhibit the same colour-sequence and the same variation in width as in the case of Lloyd's fringes dealt with above. Unfortunately, however, for want of a plane-parallel glass plate of suitable thickness, the writer has not yet been in a position to verify this result.

SECTION II — DISPERSION OF WHITE-LIGHT FRINGES IN A WEDGE-SHAPED PLATE BY OBSERVATION THROUGH A PRISM.

The peculiar dispersion of the achromatic band described in the previous section led the writer to carefully examine whether the same phenomenon is not taking place in the case when the white-light interference fringes formed by reflection from a 'thin plate' are viewed through a prism. Newton had found that in this case, not only do the fringes appear in that part of the field where without the prism mutual overlapping of the different colours had produced uniform illumination but that their number is greatly enhanced and he sometimes estimated this to be more than a hundred¹. The formation of these visible bands at unusually large thicknesses of the plate is easily understood, for it depends indeed upon precisely the same principles as the shift of the achromatic band produced by a retarding plate. But the explanation of the increased number is not so obvious, more specially in the case of a thin plate bounded by plane surfaces inclined to one another at a small angle. Referring to this wedge-shaped plate, the late Lord Rayleigh remarks² that even when viewed through a prism, the succession of colours in white light and the number of perceptible bands should remain much as usual, because unless the fringe-width changes from place to place, no relative shifts of the various colours can anywhere make the widths of the bands the same for all parts of the spectrum—a condition absolutely necessary for the formation of a *truly achromatic system* of fringes. He, therefore attributes this phenomenon observed by Newton to the curvature of the surfaces of the plate and the consequent non-uniformity of the angle between them.

But it would appear from the experiments described below that this view of the case is hardly satisfactory, for even in the case of a wedge bounded by the plane surfaces of two interferometer plates, we do actually observe a considerable increase in the number of fringes. Although there is no particular difficulty in seeing these fringes in the usual manner, it is much more convenient to mount the wedge at the focus of a collimating

¹ See quotation on page 311, Rayleigh's Sc. Papers, Vol. III.

² Scientific Papers, Vol. III, p. 313.

lens and to view the fringes by means of a telescope. The prism is placed in front of the telescope and by the suitably adjusting the inclination of the prism and the focus of the telescope, a large number of fringes are brought into the field of view. The refracting edge of the prism should be towards the thicker side of the plate.

It must be admitted that these fringes do not by any means constitute a completely achromatic system of bands and perhaps Lord Rayleigh may be quite right in denying the existence of such a system in the case of a true wedge¹. But all the same, there is in the present case a real increase in the number of perceptible fringes. The colour distribution was found to be exactly similar to what has been described in the case considered in the previous section and it was evident that here also there must be the same dispersion of the achromatic band. The width of the bands too, was not uniform and as was expected it decreased slowly from the red to the blue side.

To test the matter further, the slit of a direct vision spectroscope was placed at the focus of the observing telescope and the spectrum of the successive bands was examined. It was found to be crossed by numerous dark bands except for a narrow region free from bands on either side of which the dark bands gradually crowded in on each other. This region in the spectrum accordingly represents a group for which the visibility of the fringes is best in the part of the field under observation. As the spectroscope was moved along the bands, it was found that the position of this group slowly shifted from one end of the spectrum to the other. But probably a better idea of this is obtained when the spectroscope is turned round and its slit placed across the bands. We have in this case the various spectra of the successive bands arranged side by side and a series of beautiful curved bands appear in the spectrum, by observation of which it becomes evident at once that the region in the field at which the fringes are stationary and the visibility is accordingly best, is different for different groups in the spectrum.

That the region of best visibility of the fringes is dispersed to

¹ Reference may be made to the investigation of Mascart (*Traité de Optique*, Tome I, p. 412). The change in the apparent width of the fringes seen through the prism is a factor to be also taken into consideration.

different parts of the field can be easily seen on investigating the effect of the prism by exactly the same method as used by Rayleigh¹ in the case of a plate with cylindrical surfaces. If we choose the point of contact as the origin of x , the thickness of the wedge may be taken to be

$$t = bx$$

where b depends on the inclination of the surfaces. The black of the n^{th} order for wave-length λ occurs when

$$\frac{1}{2}n\lambda = bx$$

$$\text{or } x = \frac{n}{2b}\lambda$$

$$\text{So that } \frac{dx}{d\lambda} = \frac{n}{2b}$$

The n^{th} band formed actually at x is seen displaced under the action of the prism. The amount of the linear displacement z is proportional to the distance D at which the prism is held, so that we may take approximately

$$\frac{dz}{d\lambda} = -\beta D,$$

β representing the dispersive power of the prism. The condition that the n^{th} band is stationary for small variations of λ , is accordingly

$$\frac{d(x+z)}{d\lambda} = 0$$

$$\text{i.e. } \frac{n}{2b} = \beta D$$

$$\text{or } t = 2b\beta D$$

. Now, in the case of a prism taking Cauchy's law of dispersion, β is proportional to λ^{-1} , so that we can put $\beta = \frac{2M}{\lambda^3}$

$$n = \frac{4bMD}{\lambda^2}$$

and consequently $2MD$

It is thus seen that the region of best visibility of the fringes is different for different portions of the spectrum; for example, if

¹ Scientific Papers, Vol V, p 427.

for red light in any case $n=20$, the value of n would be 160 for the violet and we should be able to see about a hundred fringes.

An objection might be raised that all the fringes obtained in the above manner are coloured whereas according to Newton, where they seemed most distinct, the bands were only black and white successively without any other colours intermixed, though, in other places, they were undoubtedly coloured. But there is no real difficulty in explaining this apparent contradiction, if we remember that where they seem most distinct, the achromatisation has taken place for the brightest central portion (greenish yellow) of the spectrum. The colour of the rest of spectrum which forms a back-ground of uniform illumination for these fringes is not different from the colour of the maxima and what the eye perceives in this part of the field is merely the fluctuation of the intensity. In this connection it may be useful to recall the observation of Lord Rayleigh with reference to the achromatisation of Lloyd's fringes by a prism for the yellow-green part of the spectrum, where he says, "It is remarkable that so little colour should be apparent, on direct inspection of the bands" "It would seem," he adds, "that the eye is but little sensitive to colours thus presented, perhaps on account of its own want of achromatism."

III.—SUMMARY.

1. When a retarding plate is introduced in the path of one of two interfering beams, e.g. in Lloyd's experiment, the interference fringes formed in white light usually appear to shift as a whole without any change in their number or appearance, except that for the central or achromatic band the shift is slightly greater. If, however, the retarding plate is one of glass immersed in a liquid of nearly equal refractive index, these fringes are found to increase considerably in number and any attempt at partially monochromatising the light by interposing coloured screens actually *reduces* instead of increasing this number. There is left no band which may even approximately be described as central and the width of the fringes too is not constant but varies continuously from one end of the field to the other. This is shown to be due to what may be called the dispersion of the achromatic band which causes different

¹ Rayleigh, Sci. Papers, Vol. III, p. 300.

groups of waves in the spectrum to produce the maximum visibility of the fringes in different parts of the field

It is also probable that the increase in the number of white light fringes observed by Wood on introduction of sodium vapour into the path of one of the beams and which does not appear to have been explained, is also caused by a similar dispersion

2 Newton had observed that the number of white-light fringes seen in a thin plate is considerably increased by viewing them through a prism. This phenomenon was explained by the late Lord Rayleigh as being due to the formation of an achromatic system of fringes, the necessary condition for which being that the thin plate should be bounded by curved surfaces. And according to him, this phenomenon could not be expected in a truly wedge-shaped plate. The present writer has, however, actually observed it even in the case of a plate of air formed between two interferometer plates, and has shown that an achromatic system of fringes is not needed to explain Newton's observations. The dispersion of white-light fringes referred to above is sufficient in this case as well, not only to explain the enhanced number of fringes but also to give a colour distribution which appears to correspond almost exactly with Newton's observation.

3 It is to be noted that both the cases dealt with in this paper serve to emphasise and illustrate the point of view from which interference phenomena in non-homogeneous light ought to be regarded and on which Schuster rightly laid so much stress. That considerable simplicity is gained by thinking in terms of the *groups* of waves and of the *group*-velocity is perhaps best illustrated by the fact that in the case of the retarding plate discussed, the enormous shift of the fringes at the stage of equality of refractive indices of the plate and of the liquid, and the zero shift at a different stage do not require elaborate explanations and it follows as a matter of course that the shift ought to be zero at the stage of equality of group-velocities.

The writer has much pleasure in expressing his best thanks to Prof. C. V. Raman for his valuable suggestions in the course of the work.

CALCUTTA,

The 21st March, 1921.

VII. On the Beating Tones of Singing Flames.

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(Plates II and III)

I —INTRODUCTION

The maintenance of steady vibrations of the air-column in a cylindrical tube by the intermittent supply of heat in the well-known experiments with 'Singing flames' has been the subject of several enquiries from the earliest times by Chladni, Faraday, Tyndall and Sondhauss. Lord Rayleigh¹ has given a theory which is sufficient in a general way to explain the experimental facts formulated by Sondhauss.² Coming to the more recent work on the subject, it appears that the phenomena of singing flames are not so simple as might be supposed from the works of the early investigators. Wurschmidt³ has studied both theoretically and experimentally the notes produced in the singing tube. The main conclusions arrived at in his paper are that the notes emitted are not those which might have been produced by the surrounding tube treated as a pipe open at both ends, and that the frequency of the various notes depends upon the length of the flame and its position in the tube, conditioned by the unequal distribution of temperature in different parts of the tube. G. Athenesiadis⁴ has described a singing flame which gives out several sounds simultaneously and specially a flame which responds to two tones, one proper to that of the jet and the other depending on the tube used to enclose it. At this stage of double-sound he appears to have

¹ Scientific Papers, Vol. I, p. 350. Vide also Barton's Sound, 1914, p. 351.

² Pogg. Ann. 109, p. 426. ³ Verh. Deutsch. Phys. Gesellsch., 1916, p. 444.

⁴ Comptes Rendus 146, 1908, pp. 513-534.

observed a decrease in the flame as the result of reinforcement of sound proper to the tube.

While working on this line, the vibrations of the singing flame have been observed to present a novel appearance when the flame length is so adjusted as to be intermediate between the stages when the fundamental of the tube on one side and the first overtone on the other are most prominently brought out. This and the effect of different lengths of the flame on the nature of the maintained motion have been overlooked by Athenesiadis although the conditions of his experiment as regards the orifice and the tube seem to be indetical with that used by the author. The most striking effect is the peculiar throbbing appearance of the flame and the rythmic variation in the intensity of the note emitted at this stage. The subject of the present paper is a study of some of the peculiarities of this form of vibration of the singing flame which gives rise to beating tones.

Recently I have secured an extensive series of photographs of the flame, so as to bring out the rythmic variations in the form of its vibration as well as the different phases in the motion of the components of the flame, under varying conditions of pressure and flame length, some of which are reproduced in Plates II and III. The coal-gas flame which shows the features more beautifully, being not sufficiently actinic, acetylene gas was used instead and gave satisfactory results but for the accumulation of carbon on the nozzle liberated by the burning of the gas which altered to some extent the character of the vibration when the accumulation was too great. This was avoided by occasional breaking off a portion of the tip of the nozzle tube so as to leave a clean bore every time. The photographs reproduced in the paper were taken with a Zeiss lens of focal length 5 cm. on moving photographic plates.

II — EXPERIMENTAL METHOD AND RESULTS

A glass tube about a metre long and 2 cms. in internal diameter is fastened vertically on a stand so that its lower end is at a sufficient height above the table. One end of a glass tube $\frac{1}{2}$ cm. in internal diameter and 20 cms. long is drawn out to a fine jet of diameter 1 mm. at the end and the tube is connected to an air tight bottle by a rubber tube and a bent glass tube fitting into the cork at the mouth of the bottle. The bottle is kept in connection



Fig 1



Fig 2



Fig 3



Fig 4



Fig 5



Fig 6



Fig 7



Fig 8

with the gas tap, so that by adjusting the tap the amount of gas supplied to the flame can be regulated. The flame, being lighted, is introduced into the wider glass tube from below so that it is about $1/10$ of its way up the tube, when it begins to sing.

The Fundamental and the Octave in the Vibration.

On introducing the flame (which to begin with, may have a convenient length of about 2 cms) into the tube, the flame takes up a symmetrical appearance and emits the fundamental of the tube nearly free from overtones at a height about $1/13$ of the tube. That the tone emitted here is the fundamental of the open tube on the assumed mode of stationary vibration with a node at the middle, has been verified with a sonometer tuned to a known pitch, e.g. it has been calculated that whereas the fundamental frequency for the particular tube used is 127, the pitch actually found is 125.

On reducing the flame slightly the higher harmonics are emitted along with the fundamental and can be heard with the unaided ear. This is shewn in the flame picture (Fig 1, Plate II) in which the presence of the fundamental and the octave is clear. On very slightly reducing the flame length, the beating tone corresponding to the throbbing stage of the flame appears. This is described more fully below.

Reducing the gas supply still further, the flame for a moment becomes silent and then the octave alone bursts out with a symmetrical non-luminous flame, the corresponding pitch lying at about 254.

The Throbbing Stage.

In the throbbing stage of the flame, which comes in under conditions described above, the steady vibration of the flame is replaced by a throbbing with beats in which the audible and the visible effects keep exact time. The nature of the flame undergoes profound modification, for the single flame corresponding to the previous stage becomes double in some cases and triple in others, of which each component is in up and down motion relative to the others. On examining with a revolving mirror, cyclical variations in the amplitude of the different constituent parts of the flame are clearly observable, which are reproduced in Plates II. and III. Figs. 4 and 5 (Plate II)—shew the vibrations of a

long flame with three components, the middle component being in phase with the primary. The constant periodicity of the beats is very marked in Fig 5 (Plate II)

Fig 3, Plate II—shews the double flame, the beating octave being shewn by the smaller flame at the bottom, which waxes and wanes at epochs as shown also in Figs 7 and 8 (Plate III). Fig. 8, Plate III, shews a small flame exhibiting the same effect; one cycle and halves of two following one after another. Fig 2, Plate II and Fig 6, Plate III, shew the nature of beats shewn by a small flame in which the octave is powerfully maintained

The Overtones

The fundamental tone given out at this stage is accompanied by a series of overtones of which the first four can be clearly heard. By suitable adjustment of the pressure and the length of the flame, higher harmonics of the motion of the flame and the tube can be brought into prominence, and the throbbing character of the flame can be made more complex than that indicated above, e.g., it has been noticed that with a flame 4 cms. long, the component with the smallest amplitude bends at its top towards the side of the tube, while it is exhibiting the cyclical variation in its amplitude. Again in the case of very small flames, exhibiting the effect, the top of the flame visibly quivers, while the lower part remains almost steady. It is worthy of remark here, that the beating tone is replaced by a steady flame without the cyclical variation of intensity, if the amount of gas supplied to the flame be slightly reduced or increased, the octave being strong in the former case and the fundamental in the latter.

Effect of position of flame in the tube.

The general effect of raising up the flame in the tube while singing is to bring in the higher harmonics, till the characteristic throbbing flame is obtained. On further raising, the flame goes out when it is about $1/7$ of its way up the tube. There is a lower limit of the position of the flame below which no singing can be obtained. This is about 9 cms. in the case of a tube 130 cms. long.

Analysis of the note by means of resonators


It is of interest to examine what particular tones in the sound given out by the throbbing flame are shewing the cyclical variation

attendant upon the sensation of beating produced. This point has been carefully examined in the case of the gas flame with the Helmholtz resonators, which shew that the principal fluctuations in the motion are in the amplitude of the second harmonic while the sound is of a highly compound character. The fundamental which is feeble is not fluctuating and so also is the third harmonic. The fourth harmonic is found to fluctuate with a periodicity of that of the second, which in one particular case was $1/6$ of a second.

III.—SUMMARY AND CONCLUSION.

Cyclical forms of vibration in the singing flame which are produced by adjustment of the flame length, so as to be intermediate between the stages when the fundamental on one side, and the octave of the motion on the other, are strongly brought out, have been experimentally studied and photographed. The visible effect of this form of vibration is the throbbing motion of the flame accompanied by beats in the octave. The phenomenon is determined mainly by the size of the flame (as determined by the quantity of gas supplied) and its position in the tube.

The experimental investigation was carried out in the University College of Science at the suggestion of Prof. C. V. Raman to whom the author wishes to express his best thanks for many valuable criticisms in the progress of the work.



water. They appeared to be of hyperbolic form, the bows lying successively within each other. The two inner ones had the same colour sequence, that is red without and violet within, while the third which is the faintest of the three, had the opposite colour sequence. All three of them lay along the same axis.

The remarkable feature about the bows which was noticed was that as the sun gradually rose, the positions of the bows were continually changing, the innermost one gradually receding further and further away from the middle bow. Further, the further arms of the hyperbolae got gradually closer and closer till after some time it was difficult to decide whether these figures were parabolae or hyperbolae.

On searching through the literature of the subject I found, the mention of a double horizontal bow of similar form by J. Dechant in the Proc. of Vienna Academy for June 1910. The geometry of the form of the primary horizontal bow has been worked out by Otake in the Tokyo Proceedings, 1917. I shall endeavour here to explain the form of the other two bows and the other phenomena which appear along with it. Now regarding the cause of the phenomenon, I noticed that glistening dew drops were floating on the surface of the water, most probably on an oily and sooty layer on the surface of the water. It is the individual particles of soot which apparently served as condensation nuclei for the dew as the temperature gradually diminished during the night. I have tried to notice the phenomenon in other tanks in the maidan but though every one of them showed it to a certain extent, none showed it so well as the tank I have mentioned just now. My colleague and friend Mr. Satyendra Nath Bose also saw just a coloured band of light on the College Square tank, probably a portion of one arm of a hyperbola. The portion of the water surface lying between the primary and the secondary was remarkably dark and on careful observation, 3 to 4 bands of varying intensity could be seen inside the primary bow. These are the so-called supernumerary bows, explained by the theory of Airy.

Regarding the innermost bow, having the colour sequence same as that of the primary, it is to be remarked that it is much brighter than the secondary but less bright than the primary.

The geometrical theory of the rainbow is very well known as

due to the twice refracted and internally reflected beam of light from the water drops

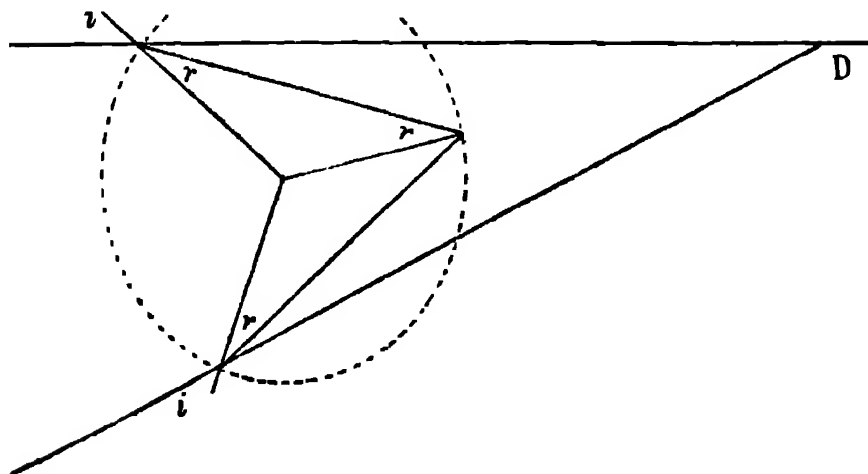


FIG 1.

$$D = 2 (i - r) + \pi - 2r$$

$$D = 2 (i - r) + n (\pi - 2r)$$

The angle of incidence of the rays which suffer minimum deviation is given by

$$\cos i = \sqrt{\frac{\mu^2 + 1}{n^2 + 2n}}$$

taking $\mu = \frac{4}{3}$

n	Red	Violet
1	$\pi - 42^\circ 1$	$\pi - 40 22$
2	$\pi - 129 2$	$\pi - 125 48$

hence the primary bow marks an angle of

Violet	Red
41°	43°

and the secondary bow

Red	Violet
51°	54°

with the direction of the source The innermost bow, as has been noticed by J. Dechant is due to the rays of sun getting inside the

plate of twice the thickness. A similar result should be true for any crystal cut symmetrically with respect to the optic axis.

As an additional illustration of the theory of Haidinger's rings in crystals, the writer has recently studied the form of the Haidinger's rings in parallel plates of quartz. Three plates (each 5 mm thick) accurately figured by Messrs Adam Hilger were secured of which one was cut perpendicular to the optic axis, one parallel to it and one at an angle of 45° . For the present, observations have been made with the first two plates only. The Haidinger's rings as seen by the reflected light of a Cooper-Hewitt mercury-vapour lamp in the plates cut parallel and perpendicular to the axis respectively showed a remarkable difference. In the latter case, the rings were very clearly seen, in the former case, they were in general very confused. Further, when the usual arrangement of holding a glass plate at an angle of 45° above the crystal for observing the rings by reflection was adopted, it was found that in the case of the quartz cut perpendicular to the axis, rotating it in its own plane produced no effect on the rings, whereas in the case of that cut parallel to the axis, the rings were very clearly seen in four positions of the crystal and were extremely confused in the four intermediate positions. The reason for this becomes evident on remembering that the light is polarised by reflexion at the glass plate held at 45° . It was found in fact, that the angular positions of the rings were different when the optic axis lies in and at right angles respectively to the plane of incidence of the glass plate. In these positions, the rings were clearest, and in the intermediate positions, the confusion was a maximum.

The plates were then silvered on both sides and the Haidinger's rings observed by directly transmitted light. In this way, sharp rings similar to those observed with a Fabry-Perot etalon may be observed. The satellites of the green mercury lines could be easily seen, and there was a great difference in the phenomena observed with glass and quartz mercury vapour lamps respectively.

With the quartz plate cut perpendicular to the axis, only one set of rings was seen near the centre of the field, but at a greater angular distance from the centre of the field the bifurcation of the rings due to the double refraction in the quartz could be distinguished. It is, of course, well-known that quartz is an

Fig 3

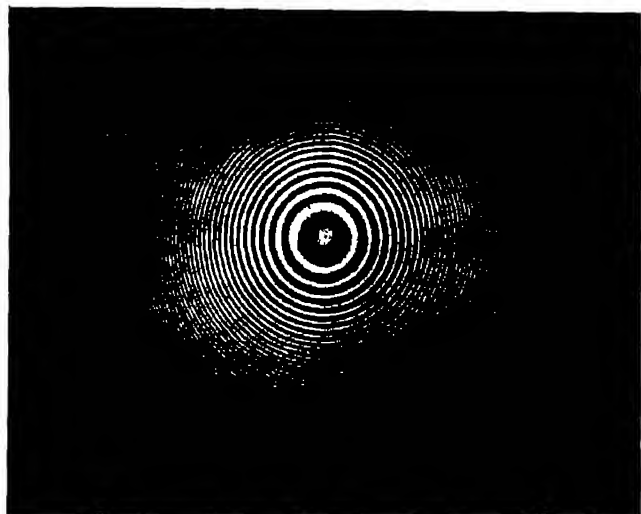


Fig 4

Fabry Perot Rings In Quartz

optically active crystal and that a plane-polarised ray entering along the axis divides up into two circularly polarised rays travelling with two different velocities. It may therefore seem at first sight be surprising that even very near the direction of the optic axis, the rings do not show a bifurcation. It must be remembered however that one of the interfering rays has to pass twice through the crystal in opposite directions and hence the emergent ray is polarised in the same way as the incident light, and we get only one set of rings.

With the silvered quartz-plate cut parallel to the axis, two sets of rings are seen throughout the field. They are widest apart along a system of hyperbolic arcs which are evidently identical with the form of the isochromatic lines in polarised light of a plate of twice the thickness. The rings are therefore least clearly seen along these hyperbolic arcs.

Photographs of the Fabry-Perot rings in the silvered quartz-plates are reproduced as Figs. 3 and 4 in Plate IV. The form of the hyperbolic arcs of minimum visibility of the rings is indicated in Fig. 4. The great difference of the clearness of the rings in the two plates, due to their doubling in the latter can be clearly seen from the reproductions.

Further investigation of the subject, especially with the obliquely cut plate appears desirable. In this connection reference may be made to a paper on the Quartz Lummer-Gehrcke Plate by Takamine in the Proceedings of the Tokyo Physico-Mathematical Society, Vol. 8, page, 296, 1915.

IX. On Quetelet's Rings in Mica.

By **Nihal Karan Sethi, D.Sc., Professor of Physics and C. M. Soganl, M.Sc., Asst. Professor, Benares Hindu University.**

(Plates V and VI.)

CONTENTS

- I —Introduction
- II —Observations in Ordinary Light
- III —Explanation of the Phenomena
- IV —Observations in Polarised Light
- V —Summary and Conclusion

I —INTRODUCTION.

When a distant source of white light is viewed by reflection at a sheet of mica of which the front surface is covered by a thin translucent film, the image of the source appears surrounded by gorgeously-coloured rings, the intensity of which is greatly enhanced by silvering the rear surface of the mica. The phenomenon is of the same nature as the well-known diffusion rings or Quetelet's rings exhibited by a dimmed mirror, but the use of the mica for the experiment gives rise, as has been pointed out in a recent paper¹ by Prof. C. V. Raman and Mr. G. L. Datta, to certain very interesting effects. If a fairly thin sheet of mica be employed, the rings are very broad and at the same time well-defined, and this makes it possible to easily observe them even when the light is incident on the sheet at large obliquities, and thus successfully to verify an effect which Stokes² had predicted from theory, but was himself unable to notice, namely that the Quetelet's rings observed at increasing angles of emergence at first become narrower and narrower, but widen again after reaching a minimum width and

¹ Phil Mag. XLII, November 1921.

² Mathematical and Physical papers, Vol. III, pp. 155-196.

become very broad at grazing emergence. But apart from this, the specially interesting feature of the Quetelet's rings in mica is their composite character which arises from the doubly-refracting property of the plate. The coloured rings are not uniformly visible over the whole field of observation, but show regions of maximum visibility separated by curved loci of minimum visibility along which the rings appear discontinuous or dislocated, the bright rings on one side of a line of minimum visibility appearing to run into dark rings on the other side and vice-versa. The phenomenon is somewhat analogous to that described in regard to Haidinger's rings in mica by Chinmayanandam¹ but differs from it in that in the present case it is not necessary to use highly monochromatic light to observe the phenomenon and further that it varies as the angle of incidence of the light is altered. The present investigation was undertaken at the suggestion of Prof Raman in order to study the phenomenon more closely and to put forward a theoretical explanation.

II —OBSERVATIONS IN ORDINARY LIGHT

Though Quetelet's rings can be seen with white light, it is of advantage to use approximately monochromatic light so that the field over which the rings are distinct may be as large as possible. The observations described in the present paper were made with sunlight, the region of spectrum made use of being, however, considerably restricted with the aid of a monochromator. The mica employed was of the muscovite variety with an apparent angle of about 70° between the optic axes, and the back surface of this was heavily silvered. This resulted in greatly enhanced brilliancy of the rings and made it possible to observe them at much larger angles of scattering. For the scattering film, a thin film of ammonium chloride deposited by volatilization has been used throughout.

Under these conditions, by working in a darkened room and properly shielding the eye from extraneous light, it is possible to observe as many as 70 or 80 rings, and the lines of minimum visibility can be seen even at normal incidence. The appearance of the lines in this case is similar to that of Haidinger's rings and is indicated in Fig 5.

The rings themselves are nearly circular or elliptical and the lines of minimum visibility possess approximately the shape of hyperbolae. There are also, as in Haidinger's rings two series of these curves with their axes nearly at right angles to each other and respectively parallel and perpendicular to the plane containing the optic axes. These are fixed relatively to the mica and rotate unchanged in position with respect to the centre of the ring system as the crystal is rotated in its own plane. And as in Haidinger's rings, the general form of these curves also does not vary much with the wave-length of the light or the thickness of the crystal, but their actual dimensions and position depend upon both. It may be noted, however, that the positions of these curves are not

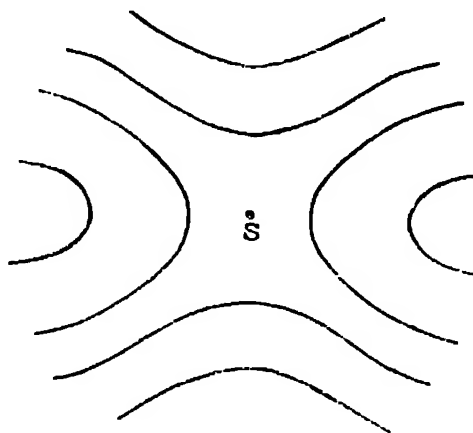


FIG 5

always identical with those of the corresponding curves in Haidinger's rings observed in the same plate with light of the same wave-length.

But when the light is made to fall obliquely on the plate and the reflected image of the source does not coincide with the centre of the ring system, the above-mentioned fixity of the curves with respect to the mica disappears, and as the mica is rotated not only do they change in position but they also appear to grow or diminish in size. Yet their axes always remain fixed in the same directions as in the case of normal incidence.

The most interesting and striking facts are, however, revealed, when the incidence is such that the regularly-refracted rays nearly

coincide with the direction of an optic axis. When this coincidence is exact, the curves of dislocation no longer all have the form of hyperbolae but some of them are closed curves surrounding the direction of the optic axis, and the reflected image of the source. Fig. 1 in Plate V corresponds to this position. Though it does not include the entire field of view as seen with the eye, two complete closed curves will be seen there, together with a third curve which is not closed. It will be noticed that these strongly resemble the isochromatic curves seen in biaxial crystals in convergent polarised light.

If now, the direction of incidence is gradually altered, as for example by slowly rotating the mica in its own plane these curves appear to increase in size and alter their form till they assume

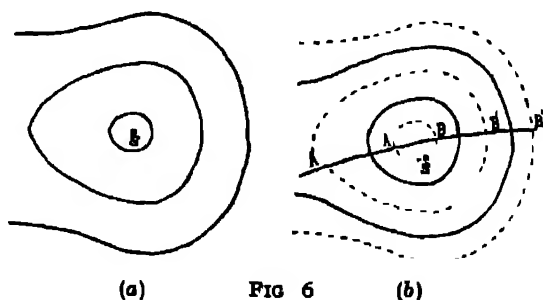


FIG 6

the curious appearance shown in Fig 2 in Plate V, and represented in Fig. 6 (b), by full line. Fig 6 (a) represents the previous case.

We still find closed curves but they are now crossed by an additional line of dislocation, more or less straight in form, and the visibility of the rings is bad in considerable regions round the crossings. On a further change in the direction of incidence the original form of closed curves is restored, but the reflected image of the source, S , is no longer at their centre. The same appearances repeat periodically as the change in the direction of incidence is continued.

Fig 3 in Plate VI shows the curves obtained when the plane of incidence is nearly perpendicular to the plane containing the optic axes.

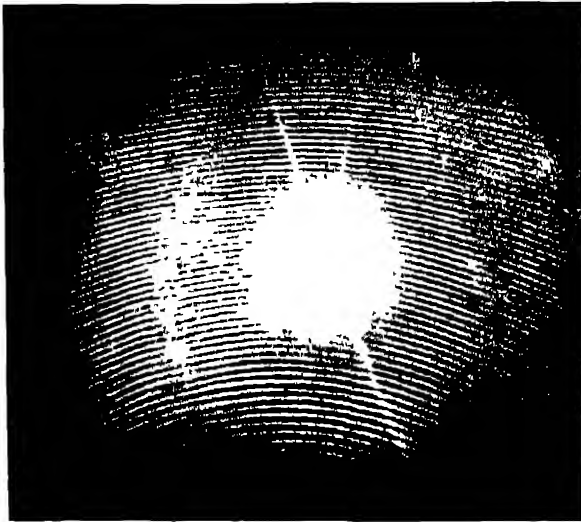


FIG. 1



FIG. 2.

III.—EXPLANATION OF THE PHENOMENA.

According to the theory put forward by Stokes,¹ Lommel² and Exner,³ the interferences in Quetelet's rings in the case of isotropic media like glass and air are due to the two sets of rays diffracted at the dimmed surface, in one case at entry and in the other case at emergence, namely the scattered-transmitted and the transmitted-scattered rays. In this simple case only a single system of circular rings is obtained.

In the case of doubly-refracting substances like mica, however, instead of a single transmitted-scattered and a scattered-transmitted ray, there will correspond to a given direction of scattering two rays of each set as represented diagrammatically in Fig. 7

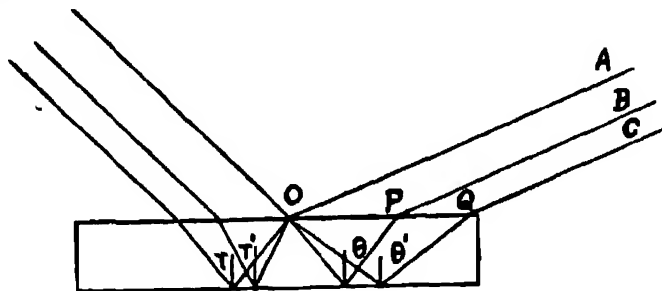


FIG. 7.

In this figure, there are two transmitted-scattered rays along OA; and PB and QC are the two scattered-transmitted rays. And each of these is polarised. According to the well-known Fresnel-Arago laws of interference of polarised light, interference between two or more rays of polarised light is possible only when all these rays are derived from the same polarised beam. Let us therefore resolve the incident unpolarised beam into two components polarised in the principal directions. Each one of these components will give rise to rays capable of interfering with each other but not with the rays derived from the other component. We should therefore consider them separately.

Taking first one of these components only we get a single

¹ *Loc. cit.*

² *Ann. der Phy.* Vol VIII, p 193 (1879).

³ *Sitzungsberichte of the Vienna Academy*, XC, p 827 (1884) and *Ann der Phy*, Vol. IX, p 339 (1880).

transmitted-scattered ray along OA together with scattered-transmitted rays both along PB and QC . The vibrations in the rays PB and QC are perpendicular to each other, but neither of these is in general parallel to the vibration in OA , which may, however, be further resolved into two perpendicular components parallel respectively to the vibrations in PB and QC . One component will then interfere with PB and the other with QC , giving us the two systems of rings

$$(a) \delta_1 = 2l (\mu_0 \cos r - \mu \cos \theta)$$

and

$$(b) \delta_2 = 2l (\mu_0 \cos r - \mu' \cos \theta')$$

where l is the thickness of the mica, r , θ and θ' are the angles indicated in Fig 7, and μ_0 , μ and μ' are the refractive indices along the directions corresponding to the rays OA , PB and QC respectively. As the acute bisectrix of the angle between the optic axes is very nearly normal to the surface of mica, the refractive index is the same after reflection as before it. These systems of rings, it may be noted, are polarised in perpendicular planes and consequently are independent of each other.

The other component of the incident light will similarly give rise to two more systems of rings

$$(c) \delta_3 = 2l (\mu_0' \cos r' - \mu \cos \theta)$$

and

$$(d) \delta_4 = 2l (\mu_0' \cos r' - \mu' \cos \theta')$$

The rays which produce these rings (c) and (d) being incapable of interfering with those which produce (a) and (b), we have now not one system of rings as in isotropic media, not even two as in Haidinger's rings in a doubly-refracting crystal but actually *four* absolutely independent systems of rings

Following Chinmayanandam's method, it can be easily shown that when θ and θ' are not large, these rings are all elliptical in form, the equation of n th order rings being respectively

$$(a) c^2 x^2 + a^2 y^2 = h \left\{ v_0^2 - \frac{a^2}{4l^2} (n\lambda - 2l\mu_0 \cos r)^2 \right\}$$

$$(b) b^2 x^2 + c^2 y^2 = h \left\{ v_0^2 - \frac{b^2}{4l^2} (n\lambda - 2l\mu_0 \cos r)^2 \right\}$$

$$(c) c^2 x^2 + a^2 y^2 = h \left\{ v_0^2 - \frac{a^2}{4l^2} (n\lambda - 2l\mu_0' \cos r')^2 \right\}$$

$$(d) b^2 x^2 + c^2 y^2 = h \left\{ v_0^2 - \frac{b^2}{4l^2} (n\lambda - 2l\mu_0' \cos r')^2 \right\}$$

where a , b , c , are the principal velocities in the mica, v_0 is the velocity in air and k is a constant, depending on the distance of the eye from the mica. It will be seen that the rings (a) and (c) are similar ellipses with their major axis lying in the plane of the optic axes, while rings (b) and (d) are also similar ellipses but with their major axis in the perpendicular direction

The visibility of these rings will be minimum wherever the maxima due to any one system coincide with the minima due to any other. There are thus six possible curves of minimum visibility given by the following equations —

$$\delta_1 - \delta_2 = 2t(\mu' \cos \theta' - \mu \cos \theta) = (2n + 1) \frac{\lambda}{2} \quad \dots \quad (1)$$

$$\delta_3 - \delta_4 = 2t(\mu' \cos \theta' - \mu \cos \theta) = (2n + 1) \frac{\lambda}{2} \quad \dots \quad (2)$$

$$\delta_1 - \delta_3 = 2t \left\{ (\mu_0 \cos r - \mu'_0 \cos r') - (\mu \cos \theta - \mu' \cos \theta') \right\} = (2n + 1) \frac{\lambda}{2} \quad (3)$$

$$\delta_2 - \delta_4 = 2t \left\{ (\mu_0 \cos r - \mu'_0 \cos r') + (\mu \cos \theta - \mu' \cos \theta') \right\} = (2n + 1) \frac{\lambda}{2} \quad (4)$$

$$\delta_1 - \delta_3 = 2t(\mu_0 \cos r - \mu'_0 \cos r') = (2n + 1) \frac{\lambda}{2} \quad (5)$$

$$\delta_2 - \delta_4 = 2t(\mu_0 \cos r - \mu'_0 \cos r') = (2n + 1) \frac{\lambda}{2} \quad (6)$$

It will be easily seen, however, that as equations (5) and (6) do not involve θ or θ' they do not represent any curves of minimum visibility. They are due to rings which are similar ellipses and only signify that the rings (a) and (c) as well as (b) and (d) are out of step in the whole field for certain directions of incidence. This would have altogether spoiled the visibility of the rings throughout the field, but for the fact that the rings (a) and (c) as well as (b) and (d) are not, in general, equally intense as will be shown further on.

Curves (1) and (2) are identical and can easily be seen to be the isochromatic curves observed in convergent polarised light for a plate of thickness $2t$. These are also identical with the curves observed in Haidinger's rings in the same plate.

Equations (3) and (4) can be re-written as

$$\begin{aligned} 2t(\mu' \cos \theta' - \mu \cos \theta) &= (2n + 1) \frac{\lambda}{2} - 2t(\mu'_0 \cos r - \mu'_0 \cos r') \\ &= (2n + 1) \frac{\lambda}{2} - k \quad \text{say} \end{aligned}$$

and

$$2i(\mu' \cos \theta' - \mu \cos \theta) = - \left\{ (2n+1)\frac{\lambda}{2} - k \right\}$$

which shows that curves (3) and (4) are also identical. These too are lemniscates whose poles are identical with those of the isochromatic curves referred to above, though, ordinarily, they differ in position from them.

To sum up, we are left in general with two sets of curves of minimum visibility of which the first is independent of the direction of incidence and is fixed relatively to the crystal and the second varies in position with the direction of the incident light on account of the constant ' k ' involved in their equations. We might call these the 'fixed' and the 'variable' sets respectively. For directions of incidence for which $k=n\lambda$, the two systems coincide, while for the directions $k=(2n+1)\frac{\lambda}{2}$, the curves of one system fall midway between those of the other. In consequence of this, the two systems alternately get in step and out of step, as the direction of incidence is altered. In addition to these, under suitable conditions of intensity, there may also appear for certain directions of incidence, some lines of minimum visibility corresponding to equations (5) and (6).

It may be noticed that as in the direction corresponding to an optic axis, $\delta_1 - \delta_2 = \delta_3 - \delta_4 = 0$, the order of the fixed curves increases in all directions as we move away from the point, and the visibility here is always maximum so far as this system is concerned. In the case of the variable curves, however, the point where a similar condition is satisfied is the reflected image of the source and the visibility in its neighbourhood therefore always remains maximum.

It should not be supposed, however, that both these systems will be equally visible everywhere, for the four sets of rings giving rise to them are not of equal intensity all over the field. In the region round the reflected image of the source to which alone the observations have to be confined on account of the feebleness of scattering at large angles, the principal directions of vibration corresponding to θ and θ' do not, in general, differ much from those corresponding to r and r' of the regularly transmitted light. For this reason, of the two disturbances along PB and QC

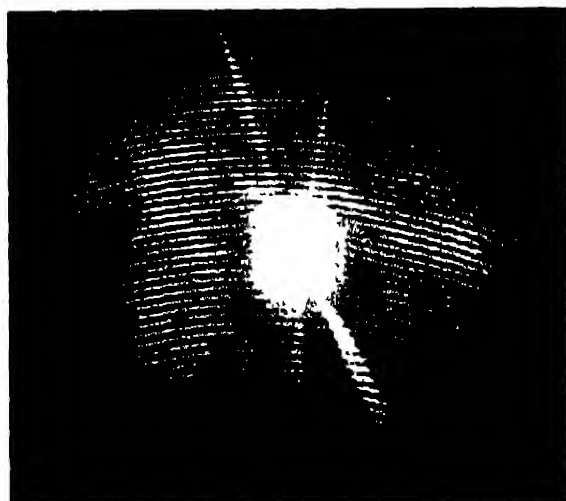


FIG. 4.

due to one of the two components of the incident light, only one will have an intensity comparable with that of OA , and therefore of the rings (a) and (b) only the ring (a), say, will be formed. Similarly of the rings (c) and (d) due to the other component, only one (d) will be visible along with (a). Thus of the two systems of curves of minimum visibility, the fixed one cannot be expected to be observed in this region. Only the variable system will be present.

If, however, the incidence nearly corresponds to the direction of an optic axis, even in the narrow region round the reflected image of the source, the principal directions of vibration change from point to point so that it is possible to find directions in which the intensities of the two rings (a) and (b) as also of (c) and (d) are comparable. Portions of the fixed curves ought to be observable in these directions in addition to the variable curves which are present everywhere, for wherever rings (a) and (d) are weak, rings (b) and (c) will become prominent giving rise to the same curve of discontinuity again. The presence of these portions of the fixed discontinuities will not, however, make any difference in the appearance of the variable curves for directions of incidence such that $k=n\lambda$ owing to the overlapping of the two systems

(case illustrated in Fig. 1) But whenever $k=(2n+1)\frac{\lambda}{2}$, these will fall between the variable curves and spoil the visibility of the rings there. It is this case which is illustrated in Fig. 2

That here k was really equal to $(2n+1)\frac{\lambda}{2}$, was verified by polarising the incident light and observing the regularly transmitted light from behind the mica with a quarter-wave plate and a nicol. In connection with this, attention may also be drawn to a very curious line of minimum visibility seen running almost straight through the middle of the closed curves. This belongs neither to the fixed nor to the variable system, but is a part of the minimum visibility represented by equations (5) and (6) and makes its appearance because all along this line, which is an isogyre running through the portions of the fixed discontinuities visible in this case, the four rings (a), (b), (c) and (d) are more or less equally strong.

IV.—OBSERVATIONS IN POLARISED LIGHT.

(a) Incident Light Polarised

In general, when the incident light is polarised no curves of minimum visibility are seen, but careful observation shows that in certain directions, there are small regions of dislocation extending barely over half a dozen rings. In the cases corresponding to Figs. 1 and 6 (a), two such portions at nearly opposite points of each curve are visible. These go on rotating round the curves as the incident plane of polarisation is rotated interchanging these positions after a rotation of the nicol through 90° and completing the round in 180° . In the special cases when the curves have the appearance shown in Fig. 2 and Fig. 6 (b) the behaviour is slightly different. When the incident plane of polarisation coincides with one of the principal directions, the discontinuities are found in the positions marked A and B in Fig. 6 (b). As the plane of polarisation is rotated, these discontinuities rotate a little and expand until at 45° nearly, the whole of the curve in Fig. 2 makes its appearance. On further rotation, the discontinuities contract again until at 90° we are left with the same original appearance.

(b) Incident Light Unpolarised and Rings observed through a nicol

Observations in this case are similar to those in case (a).

(c) Incident Light polarised and the rings observed through a nicol

For any one of the directions of incidence when the closed curves appear quite distinctly in unpolarised light, we have already seen that in every position of the polarising nicol, only two small portions of each of these curves are visible. On observing the rings through a second nicol the discontinuities are found in exactly the same positions for one particular direction of this nicol. On rotating it however, they are found to rotate round the curves interchanging their positions after 180° and not after 90° as in cases (a) and (b). At 90° , when the discontinuities occupy intermediate positions, some very interesting effects are observed. For there appears in the field of view, a dark line running along an *isogyre* through the discontinuities together with dark curves similar in form to the bright curves of minimum visibility seen in unpolarised light but falling midway between them. At the same time, the visibility of the rings becomes bad throughout the field, and but for the rings,

still discernible, the whole appearance strongly resembles that usually obtained in convergent polarised light.

For the intermediate directions of incidence which give us the complicated appearance in Fig 2, the effects observed when the incident light is polarised in a principal plane are similar though differing in important respects. We get the same rotation of the discontinuities, but this, instead of taking place along the closed curves actually visible in unpolarised light, follows the invisible intermediate curves. As a consequence of this, one of the discontinuities passes through the image of the source itself, a very interesting fact indeed. We also get a dark line and the dark curves, but these again do not fall between the curves visible in ordinarily light but coincide with them.

We will now consider the explanation of the foregoing effects confining ourselves to the two important cases when

$$(1) k = n\lambda \quad \text{and} \quad (2) k = (2n + 1)\frac{\lambda}{2}$$

(a) *Incident light polarised*

In this case when, $k = n\lambda$, the transmitted-scattered ray is evidently plane-polarised. Its vibrations may, as before be resolved into two components parallel respectively to the vibrations along PB and QC , and we shall get two ring systems with equations identical with those of (a) and (b). In the directions of scattering in which the angle between the directions of vibration of PB and QC and of the transmitted-scattered ray OA is 0° or 90° , only one of these rings will be present. In directions in which the angle is about 45° , the two rings are more or less of equal intensity and those portions of the curves of minimum visibility which lie in these directions will therefore be visible. As the plane of polarisation of the incident light is rotated, the resultant direction of vibration along OA will be rotated also and this condition will be satisfied in some other directions of scattering with the result that these discontinuities will appear to rotate round the curve as seen in unpolarised light.

When, however, $k = (2n + 1)\frac{\lambda}{2}$, although the transmitted-scattered ray OA is still plane-polarised, yet as the two perpendicular components to which it is due are in opposite phases, its phase is indeterminate and we cannot proceed as above. It is therefore necessary to consider both the components of OA separately.

This will again give us four ring systems as in the case of unpolarised light. Being polarised perpendicularly the rings (a) and (b) are independent as are also the rings (c) and (d). The rings (a) and (c) or (b) and (d) are similarly polarised and are therefore not strictly independent, but being out of step every where in the field, they may also be regarded as independent. The case is therefore identical with that of unpolarised light except that in this case the two components into which the incident light is divided are not in general equal in intensity. Thus, for example, when the incident light is polarised in one of the principal directions, only two rings say (a) and (b) will be formed. These will as before give rise to exactly the same small portions of the discontinuities which in the case of unpolarised light fall between the variable curves and spoil the visibility of the rings in that region. But when the incident light is polarised in a plane inclined at 45° to the principal directions, both the components will be equally strong and the case becomes identical in all respects with that of unpolarised light and all the lines of minimum visibility as seen in ordinary light will make their appearance. This is in complete agreement with the observations already recorded.

The effects observed when the rings are viewed through a nicol and the incident light is unpolarised can be easily explained on similar lines, if we remember that this nicol does not interfere with the actual formation of the rings but only cuts off a certain portion of the light from them and alters their relative intensities to different extents in different directions.

We will now proceed to explain the formation of the very interesting dark curves that appear when the rings are viewed through a nicol and the incident light is also polarised. We have already seen that in the case when $k=n\lambda$, the transmitted-scattered ray is polarised. The plane of polarisation of this ray is nearly the same as that of regularly transmitted-reflected ray all over the narrow field in its neighbourhood. It follows therefore that when the analysing nicol is crossed to this direction, the transmitted-scattered ray vanishes at every point, and we are left with the two perpendicularly polarised scattered-transmitted rays, the phase-difference between which is given by

$$\delta = 2t (\mu \cos \theta - \mu' \cos \theta')$$

It will be seen that this phase-difference is constant along curves identical with the isochromatic curves and is a whole number of wave lengths along curves

$$2t (\mu \cos \theta - \mu' \cos \theta') = n\lambda$$

These can be easily seen to lie between the curves of the fixed system of minimum visibility. All along these curves, the two scattered-transmitted vibrations will combine to give us a plane vibration, more or less coinciding in direction with the regularly transmitted vibration and will therefore vanish simultaneously with it. No light will thus reach us from these curves which will in consequence appear dark. The presence of the isogyric line in this case hardly needs an explanation. In the case when $k = (2n+1)\frac{\lambda}{2}$, although the transmitted-scattered ray is still polarised yet the above conditions are not satisfied except when the incident light is polarised in a principal plane. The result is that the dark curves appear fully formed in this case only.

V — SUMMARY AND CONCLUSION

1 The interesting effects due to double refraction observed in Quetelet's rings in mica by Prof C V Raman and Mr G L Datta have been studied in detail and a theoretical explanation has been put forward

2 It has been shown that in this case we have *four* independent sets of Quetelet's rings nearly elliptical in form in place of the single set of circular rings in isotropic media, and the interactions of these give rise to two different systems of curves of minimum visibility.

3. One of these systems of curves is *fixed* relatively to the mica and is identical with that observed in Haidinger's rings in the same plate. It consists of isochromatic curves or lemniscates similar to those seen in convergent polarised light. Only small portions of these curves are, however, visible because all the four ring systems are not equally intense everywhere in the field

4. The other system also consists of lemniscates with the same poles as the fixed system, but the exact size and positions of the curves of this system undergo considerable changes as the direction of incidence is altered, alternately coinciding and

getting out of step with the curves of the fixed system These curves are fully visible everywhere

5 When the two systems are out of step, an additional line of dislocation is also observed This runs nearly along an isogyre and is observable in the neighbourhood of the optic axis (Plates V and VI.)

6 When the incident light is polarised, or when the rings are observed through a nicol, the appearance is altogether different and in general only very small portions of the curves are visible in isolated localities (Fig 4 in Plate VI) These change their positions and rotate round the curves when the polarising or the observing nicol is rotated.

7 But when the incident light is polarised and the observations are also taken through a nicol, we get certain dark curves and an isogyric line in place of the usual bright curves of minimum visibility, the whole appearance strongly resembling that observed with crossed nicols in convergent light. Even these special effects in polarised light have been shown to follow easily from the theory advanced in this paper

In conclusion, the writers wish to express their cordial thanks to Prof C V. Raman for the suggestion of the problem as well as for the interest he has taken in the work

*Physical Lab , B H U ,
Benares,
The 2nd May, 1922*

X. On the Colours of Tempered Steel and other Tarnished Metal Surfaces

**By Brojendra Nath Chuckerbutti, D.Sc., Assistant Professor
of Physics, Calcutta University.**

(Plate VII)

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- I —Introduction**
- II —Experimental details**
 - (i) Preparation of metal plates
 - (ii) Microscopic observation of the plates
- III —Description of phenomena observed**
 - (i) Colour and polarisation of the reflected light
 - (ii) Colour and polarisation of the scattered light
 - (iii) Quantitative study of the scattered light
 - (iv) Study of the reflected light with a Babinet compensator
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I —INTRODUCTION

The well-known and characteristic tints that appear on a metal surface when it is heated in air, have been the subject of interest for a long time. When, for instance, a polished steel plate is heated over a Bunsen flame, rings of colour appear forming a periodic succession, somewhat in the manner of Newton's rings, and the explanation usually put forward is that they are due to the interference of the light reflected at the surfaces of a thin film formed upon the metal as the result of oxidation. In a recent paper, Mallock ¹ has questioned the correctness of this familiar

explanation On trying to polish gently a tempered steel surface, he found that there was no change in the colours observed as the film was gradually removed Thus, for instance, a blue-tempered steel remained blue throughout the process of polishing until the clear metallic surface was reached, although there was a visible change in the intensity of the reflected light

Observing the reflected colours through a nicol oriented so as to quench the reflected light as far as possible, Mallock found that as the angle of incidence is increased beyond that required for maximum polarisation, the colours changed with obliquity almost in the same manner as in case of high order Newton's rings But the thickness of the film necessary for the production of such high order rings, is far greater than that of the actual thickness of the film upon the metal surface. As the results of these observations, he concluded that "the colours must be due to some form of selective opacity depending on damped molecular periods comparable with the wave-period rather than on a structure comparable with the wave-length"

Sir George Beilby¹ has also made observations on the subject of these coloured films According to him the film is an aggregate in open formation, through which oxygen molecules can penetrate to the metallic surface underneath The colour of the film formed depends not only on the temperature to which the metal is raised but also upon the time for which the heating is continued

Recently, in a note published in *Nature*, Prof. C V Raman² has put forward a different explanation of these colours. He drew attention to the fact that the plates exhibit a colour by scattered light which is complementary to that shown by reflected light As the result of his observations on the colour and polarisation of the light reflected and scattered from the surfaces, Raman has put forward the view that the colours under discussion are in the nature of *diffraction effects* arising from a film which is not continuous, but has a close-grained structure.

Now, the theory that the colours are intrinsic put forward by Mallock and apparently supported by Beilby, presents serious difficulties and cannot be accepted. Apart from all other consi-

¹ Beilby—"Aggregation and Flow of Solids" (Sections 3 & 10).

² Raman—*Nature*, January 26, 1922.

derations, the very fact that the colours on the plate form an approximately periodic sequence, strongly suggests that they are in great part due to either interference or to diffraction, and only in a minor degree to *intrinsic* colour which cannot, according to any reasonable supposition be expected to exhibit a periodic sequence with the growth of the film. Since the observations of Mallock appear to exclude simple interference as the origin of the phenomena, we are left with the only other alternative left as an explanation, that is, that the colours arise from the scattering or diffraction of light by a granular structure in the manner suggested by Raman.

The present author took up this investigation with the object of making a detailed study of the whole phenomenon and to collect experimental evidence for a comprehensive explanation of the facts. The principal task was to obtain a set of highly polished metal plates. For in case of plates not properly polished, the colour sequence, especially of the scattered light as distinguished from that regularly reflected cannot be satisfactorily observed, and it is not possible to derive useful information with their aid. After prolonged trial, however, the necessary technique was acquired, and the problem has been thoroughly studied from various stand points, and also with plates of different metals. As has been observed by Raman,¹ copper (which, however allows a very high polish easily) shows the phenomena very beautifully and is found rather the most suitable for the different experiments.

Now, Beilby² has shown that the process of polishing a metal surface causes the surface layer to "flow" as a liquid, and thus the polished surface is that of the metal in the amorphous state, that is to say, the metal molecules are distributed at random. It is not unreasonable to suppose that the subsequent process of heating results in the formation of aggregates of these molecules, some of which are altered by oxidation. Hence the problem reduces itself to the determination of the scattering of light by

¹ Raman—*loc. cit.*

² Beilby—Hunter memorial lectures, Glasgow, 1903, page 46, also "Aggregation and Flow of Solids."

Rayleigh—(Royal Institution lecture on "Polish," March, 1901) also holds the view that the process of polishing is a molecular one.

small granules of oxidised metal formed during heating which differs from the metal itself in its optical properties. As the result of the experiments that will be described in the subsequent pages, it can definitely be asserted that the colours exhibited by heated metal surfaces are due to the *scattering of light* by the granular film of oxide formed during heating.

II.—EXPERIMENTAL DETAILS.

(*) *Preparation of metal plates*

On putting a polished metal plate upon a Bunsen flame, colours come in such a rapid succession that it is impossible to obtain an uniformly-coloured plate in this way. Moreover, the temperature of the flame being rather high, it is difficult to regulate the heating apart from uniformity, so that there is no knowing as to when to stop in order to obtain a plate, say blue, green or yellow-coloured. With a view to avoid all these difficulties a method of slow heating by an electrical heater was employed. The small metal plate to be experimented upon, was placed on a bigger metallic plate which later was placed as near as possible to the heating coils. The resistance of the coils so employed was 60 ohms and the current was run from the main switch of 220 volts. Thus the heating was slow and uniform and moreover, it gave all facilities for proper regulation. The current was allowed to run through the circuit for 5 minutes before the plates were put in position. In this way different plates were prepared both of copper and iron, which exhibited most of the colours that enter into the composition of white light. As a result of experiment, it is found that uniformity of colour is also ensured when the surface is perfectly polished and clean, quite devoid of any sort of grease. Dirty plates begin to grow high order colours at the places where dirt exists, long before the first traces of colour are seen in other parts of the surface even, when all other precautions for uniform heating are taken. In each case, colour starts at about a reddish or violetish tint which is rather difficult to distinguish on account of the surface colour of the metals. Next, the colour turns to violet in case of copper, and indigo in case of iron. Copper being further heated shows indigo, green, yellow in succession. On still further heating, rather at a high temperature the colour is almost



THE COLOURS OF TEMPERED STEEL

white and then again it starts from red, and ends in green and yellowish green. Further heating blackens the plate due to the formation of the black oxide. The colours exhibited at this repetition are very rich and gorgeous. In this stage, the formation of the surface-structure becomes visibly discontinuous and granular which, when gently rubbed, falls off here and there exposing the clean metal surface below. The iron plates exhibit beautiful blue and green colour after the indigo state. They next turn to red. The periodic recurrence of colours is beautifully observed in case of copper plates. The conductivity of the metal being high, to obtain all the colour sequences upon the same plate, a temperature gradient was set up along the surface, the far end being allowed to rest upon a block of ice while the other end was put on a Bunsen flame. Thus, bands of colour were made to travel from the hotter to the colder part of the plate on account of this temperature gradient. Such a precaution, however, is not needed in case of iron or steel. If a thin strip of these metals be taken and one end kept in touch with a Bunsen flame, the bands with periodic recurrence of colours begin to travel from the hotter to the colder parts of the plate. In this connection, it must be noted that this recurrence of colours at the second stage with all its enhanced gorgeousness is not to be observed even in case of copper in the process of slow heating. Here, after the yellow stage, the colours lose all their brilliancy. For, although, there is a re-appearance of a dull red and finally before blackening a dull greenish yellow colour, yet they can in no way stand comparison with the colours obtained by heating over a Bunsen flame.

Since the formation of the surface-structure is to be attributed to oxidation of the metal, an estimate of the thickness of the structure may be made if the plates are weighed before and after the operation. With this view the plates were polished on both the sides so as to get rid of any foreign matter that might cling to the rough under-surface. After final polish, the plate was slightly heated to expel water vapour and while hot was put inside a desiccator and allowed to cool there. It was then weighed with a good balance. After the operation also, it was put in the desiccator while hot and allowed to cool as before. From the gain in weight of the plates and also on the assumption that the structure on both sides is of the same thickness and nature, it is easy

to estimate the quantity of metal that has gone into the formation of its oxide. Thence, the dimensions of the plate and density of the metal will give the thickness of the metal layer which is oxidised. Thus it was found that in passing from the initial stage to the last green or yellow stage in the process of electrical heating, the thickness of metal layer affected increases from 5μ to 115μ . Thus the process of the formation of the structure is confined within a very thin layer of the metal surface and the metal below remains as good and pure as ever.

(ii) *Microscopic observation of the Plates*

That the structure formed upon the surface is not at all continuous, but granular, can be seen at once if the plates be subjected to a microscopic study. The difficulty lies in the fact that the granules having the metal surface at the back cannot be illuminated from below. Light from a high candle-power source incident very obliquely upon the plates, however, serves the purpose of illumination fairly well. The plates prepared during the initial stages of heating reveal a very large number of small particles quite separate from one another but sometimes forming clusters interspersed here and there with particles of bigger size. These bigger particles upon the plates at the initial stages might be due to the presence of traces of grease or to a too close formation of small particles which it is impossible for the microscope to show separately. It is not difficult to measure the size of the granules with the help of a micrometer eyepiece properly calibrated. As the colour of the plates changes during the process of heating, the particles also as revealed by the microscope in case of different plates, go on increasing in dimensions. Their diameter in the initial stages appears to be about 225μ and finally in the greenish yellow stage of slow heating the diameter comes out to be about 600μ . During the second stage of re-appearance of colours the size of the particles becomes rather big, the diameter becoming $9,000 \text{ \AA}$ U, i.e. about four times the diameter of the particles at the initial stages.

The results of heating some of the copper and iron plates are given in a table (Table I) at the end. It will be found that in case of copper, only up to the first yellow stage the heating was continued and in case of iron, the plates were heated up to the

yellowish green stage only. In column 6, the gain in weight of the plates by heating is entered in while in the last column, the results of microscopic observations are given. The size of the particles are given in terms (ka) where $k=2\pi/\lambda$ (λ being the wave length of light) and a the radius of the particles assuming them to be circular in shape.

III — DESCRIPTION OF THE PHENOMENA OBSERVED

(i) *Colour and Polarisation of the Reflected Light.*

If a beam of white light be allowed to fall upon one of the metal plates used in the present investigation, then the colour and polarisation of the reflected light vary with the angle of incidence and the thickness of the film upon the surface, in a very remarkable way. It is instructive to be able to observe the phenomena with the differently coloured films simultaneously, and for this purpose may be used one of the copper or iron plates in which the complete succession of colours has been developed by setting up a temperature-gradient between its ends. One of these plates may be simply held in the hand and the light reflected from it at various angles of incidence may be viewed with or without a nicol held in front of the eye. For quantitative determinations, the plate may be mounted up on a spectrometer table and the reflected light observed through a tube fitted with a nicol which can be taken out or put in position at will.

Viewed with the naked eye the reflected colours are most lively at or about normal incidence, and become less and less saturated as the incidence is made more oblique until finally there is so much white light reflected at the surface of the metal that no colour can be distinguished at all. With the copper plates, colours can be distinguished even at fairly oblique incidence and a remarkable *doubling* of the first coloured band may then be observed. The reason for these effects is easily made out if a nicol be held in front of the eye. Even at small obliquities, the reflected light from the thinner portions of the film shows marked changes in intensity and colour as the nicol is rotated about its axis. The thicker portions of the film on the other hand, show little change at this stage as the nicol is turned round; at more oblique incidences, however, the light reflected from the thicker portions of the film shows striking effects being less intense and more vividly coloured in one posi-

tion of the nicol (principal plane perpendicular to the plane of incidence), and more intense but less strongly coloured in the parallel position. In these two cases, beyond a certain angle of incidence which varies with the thickness of the part of the film under consideration, the colours observed in the two positions of the nicol are complementary to each other.

As the nicol is rotated, the shifting to and fro of the coloured bands on the plates may be observed, this effect being most conspicuous on the first coloured band. The relative feebleness of the colours when viewed with the naked eye, at oblique incidences is thus easily understood as due to the complementary colours of both components of polarisation being superposed on each other. The apparent doubling of the first coloured band on the copper plates is also due to this cause.

At very oblique incidences, only the thickest parts of the film exhibit vivid colour when viewed through the nicol.

(ii) *Colour and Polarisation of the Scattered Light*

It is to be remarked as a very important feature, that the films on the metallic surfaces under consideration scatter light very strongly. As a general rule it may be stated, that the colour of the scattered light when observed in directions but little removed from that of the regularly reflected light is complementary to it in colour. The behaviour of the scattered light for various angles of incidence can be very beautifully observed with a metal plate showing the complete sequence of colours as in the experiments described in the previous section. For quantitative observation, the plate may merely be held in the path of a strong beam of light and viewed directly or through a nicol. For more exact work, the spectrometer and a telescope tube fitted with a nicol may be used. It is very important that the plate before heating up should have received a high polish. Scratches and other irregularities upon the surface reflect light into the eye and thus tend to obscure the true scattered colours.

The observations of the scattered light may be divided into several headings as follows:—

(a) *Normal Incidence (of unpolarised white light).*—In viewing the scattered light with naked eye, when a beam of unpolarised white light is incident normally upon a metal plate, it is found

that the colour of the light scattered by the film passes through several fluctuations as we move our eye from the direction of the plane of the plate to the direction of the incident beam. As already remarked, the scattered light in directions contiguous to the reflected beam is complementary to it in colour. As we move away however, the colour changes. On examining the scattered light with the nicol, it is found that in directions near about the reflected beam the light is unpolarised and shows no change when the observing nicol is rotated. But in more oblique directions the changes in the intensity and colour of the scattered light becomes noticeable and at a small angle with the plate, the scattered colours show complementary tints on rotating the observing nicol through 90° .

(b) *Light polarised perpendicularly or parallel to the plane of incidence incident normally* — When a beam of white light polarised either in the plane of incidence or perpendicular to that is incident upon the plate, the scattered light very near to the direction of the reflected beam cannot be quenched in any position of the analysing nicol but it simply shows fluctuations in intensity as the analyser is rotated. But commencing from about an angle of 30° till the surface of the plate is reached, the colours can entirely be quenched by the analysing nicol, which re appear again on further rotation of the nicol.

(c) *Light polarised in any azimuth (say 45°), incident normally* — When the incident light is polarised in an azimuth of 45° with the plane of incidence, the phenomena to be observed in the scattered light with the help of the analyser is more or less the same as for light polarised in or perpendicular to the plane of incidence, the quenching of colours with the help of the analyser being more perfect as we come nearer the direction of the surface of the plate.

(d) *Oblique incidences with unpolarised white light* — As the angle of incidence increases, the beauty and diversity of the phenomena to be observed with the scattered light also go on increasing. The colour-changes become more and more frequent and in certain directions the tints change to the complementary colours when the analysing nicol is rotated through 90° . For very oblique incidences it is found that in certain directions the intensity of light in one position of the observing nicol becomes enormously great in comparison with the light observed in the perpendicular position. In case of thin films, such a direction for maximum polarisation is

found at an angle of about 100° with the direction of the incident beam (incidence about 88°) whereas, for plates containing thicker film with larger particles, such maximum polarisation may be observed in two, three or more directions.

(e) *Light polarised in any azimuth incident obliquely.*—When the incident beam instead of being unpolarised, is polarised in any azimuth, the scattered light, shows the fluctuations of colour and intensity as before. Only the colours to be observed for any suitable position of the nicols become more and more saturated. The scattered light in the field, however, cannot be completely quenched in any position of the nicol although some particular colours may completely be cut off by crossing the nicols, a slight movement of the nicols to the right or to the left causing the reappearance of the same colour. In directions near about the incident and the reflected beams the colour-fluctuation on the rotation of the analyser is very prominent.

In this connection, it is to be mentioned that the complementary nature of the scattered light observed at a very small angle with the surface of the plate, for two positions of the nicol when the light is incident normally upon the plate correspond to the observations of wood¹ and later on of Rayleigh² in case of thin film of collodion spread upon metal plates

(iii) *Quantitative Study of the Scattered Light*

All measurements and observations in connection with the experiments to be described in this section were made with a Cornu polarimeter, which is generally used in the experiments for the analysis of the polarised light. Here, the telescope tube consists of a small rectangular opening through which the light to be examined passes, a double-image-prism, and a nicol capable of being rotated about its own axis and attached to a divided circle. The double-image prism is fixed at such a distance from the rectangular opening that the two images—one polarised vertically and other horizontally—are seen one above the other. In the observation of the colour fluctuations of the scattered light as described in the previous section, the analyser is dispensed with and

¹ Wood—Physical Optics, page 172, ed 1914

² Rayleigh—Phil. Mag Vol 34, Nov 1917.
Scientific Papers, Vol 6, p 508

the colours of the two images formed by scattered light for different positions of the observer's eye as recorded by the graduated circle of the polarimeter upon which the telescope moves are observed and noted. As remarked before, in order to be able to follow the behaviour of the scattered light for quite a wide range a very oblique incidence was used in all the quantitative studies. Results for the observations on various plates and also for different directions of observation at intervals of 10° are entered into a table (Table II) at the end of the paper. The different phenomena roughly detailed in the last section will be found rather precisely put into this table. The angle θ which has been entered into the first column of this table gives the angular measure for the direction of observation commencing from the negative direction of the incident beam so that we approach to $\theta=180^\circ$, as we approach the direction of the surface of the plate when the incidence is very oblique. The next two columns give the colour for the vertical and the horizontal components of the scattered light as formed with the double image prism.

In making the following observations, the analysing nicol of the telescope of the polarimeter was put in position. The incident light was rendered monochromatic with suitable light filters. Observations were made with three different kinds of filters, viz

$$\lambda = 6290 \text{ A.U.}, \quad \lambda = 5830 \text{ A.U.}, \text{ and } \lambda = 4380 \text{ A.U.}$$

for the purpose of comparison. It was found that the results in all three cases agree on the whole, there being a shift in the positions of neutral points and in the direction of maximum polarisation as far as we should expect for the difference of wave length. So, the final graphs were plotted with the results obtained in using the monochromater for which $\lambda = 5830 \text{ A.U.}$

To start with, the zero reading of the nicol is made to correspond to its position when one of the images (say the upper one) vanishes. Then the nicol may be set in two positions on the two sides of this zero position for which the intensity of the two components will be equal. Thus, if w_1 and w_2 be the two readings for the angle of rotation about the zero position for which the intensities I_1 and I_2 of the two components are equal, we have

$$\frac{I_1}{I_2} = \frac{\cos^2 w_1}{\sin^2 w_1} = \frac{\cos^2 w_2}{\sin^2 w_2} = \frac{\cos^4 w_1 + \cos^4 w_2}{\sin^4 w_1 + \sin^4 w_2}$$

whence

$$\frac{I_1 - I_2}{I_1 + I_2} = \cos(w_1 + w_2) \cos(w_1 - w_2) \\ = \cos 2w$$

where w is the mean of the two angles w_1 and w_2 . For the sake of convenience a quantity P is chosen such that

$$P = 100 \frac{I_1 - I_2}{I_1 + I_2} = 100 \cos 2w.$$

Thus we can determine the value of P in different directions for the scattered light within the limit $\theta = 180^\circ$ to $\theta = 0$.

In the graphs of Figs. 1 and 2 the values of P are plotted for different plates the value of η for which is given near the curve

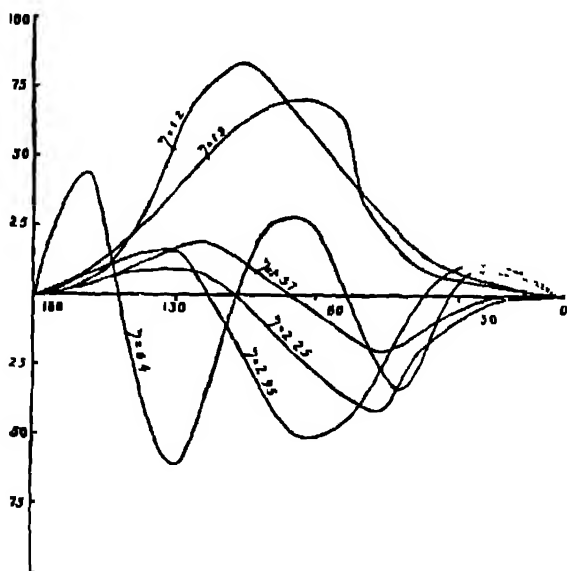


FIG. 1. Experimental curves for Copper.

Taking Fig. 1 which contains the curves for different copper-plates it will be seen that for very small particles ($\eta = 1.1$), the maximum polarisation is at an angle of 100° and there is no neutral point ($P = 0$). As the size of the particle increases, the position of the maximum polarisation also is shifted towards the incident light at first. For $\eta = 1.3$, we have the position of maximum polarisation at $\theta = 90^\circ$ and the corresponding value for P is 68, i.e.

smaller than the former value. In the last three curves, viz $\eta=1.57$, $\eta=2.25$ and $\eta=2.95$, we note many peculiarities. Each of these curves show two or more maxima and neutral points. For $\eta=1.57$, a neutral point is found at $\theta=95^\circ$, which point is found to shift towards the direction of reflected beam as the size of the particles increases. It is also to be noted that the negative values of P are rather prominent than the positive in the latter cases. In the last curve, viz $\eta=2.95$ we have two neutral points one at $\theta=120^\circ$ and the other at $\theta=45^\circ$. Hence, the experimental curve for iron will explain itself. From these observations on intensity the following are the peculiarities to be observed.

(a) The scattered light is never plane-polarised in any direction, but there is a direction of maximum polarisation for small particles ($\eta=1.2$, $\eta=1.3$), which are formed during the first stage of heating of the plates. For the smallest particles obtained by the author, the position of this maximum is at $\theta=100^\circ$.

(b) As η increases, the position of maximum first moves towards the incident beam (as in $\eta=1.30$) and then it moves back towards the 120° position, for when $\eta=1.6$ it is at about $\theta=120^\circ$ with the incident beam.

(c) At the same time with the increment in the size of the particles, a neutral point ($P=0$) appears which when $\eta=1.57$ is at $\theta=90^\circ$.

(d) Between the neutral point and $\theta=0$, the polarisation is reversed, that is, the horizontal component I_h is greater than the vertical component I_v and consequently P is negative.

(e) As the value of η increases, the position of this neutral point moves towards the direction of the reflected beam and newer neutral points originate on the other side.

That the number of neutral points ($P=0$), increases with the size of the particles, will be seen from the curve for $\eta=6.4$ in Fig. 1. This curve was obtained when light was made to be scattered by the beautiful green particles obtained during the second stage of periodic recurrence when one end of a copperplate was heated in a Bunsen flame while the other end was placed upon a block of ice with a view to maintain a temperature gradient. Altogether we have 4 neutral points in this case, at about $\theta=150^\circ$, $\theta=110^\circ$, $\theta=70^\circ$ and lastly at $\theta=40^\circ$. Beyond that point it was not possible to follow the change in intensity, as there is a general

falling off in intensity. Another peculiarity to be noticed in this case is the fact that maximum value of P both on the negative and on the positive side goes on decreasing as we move from $\theta=180^\circ$ to $\theta=0$.

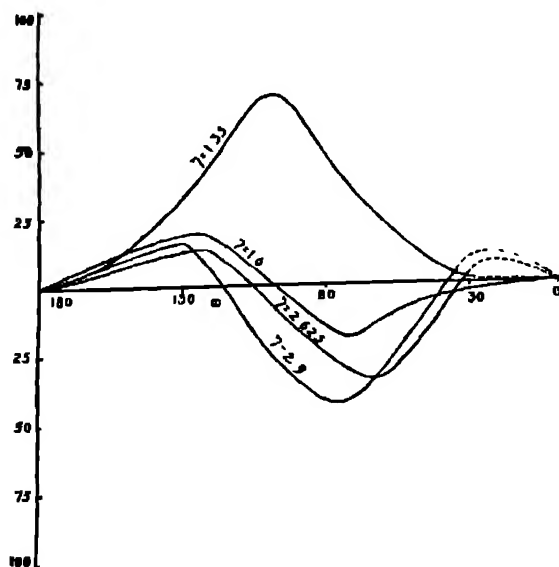


FIG. 2. Experimental curves for Iron

From a study of the complete set of curves, it is also to be noticed that the maximum value of P obtained with smallest size of particles, is the greatest of all. As the size of the particles increases and they become comparable to the wave length of light ordinary reflexion will take place. As it is a well-known fact that light cannot be perfectly polarised by reflection from a perfectly conducting sphere, finally for all values of θ , the intensity of the two components will be equal or in other words, for very big particles, the curve will reduce to a straight line given by the equation $P=0$.

(iv) *Study of the reflected light with a Babinet compensator.*

Since the condition of the polished surfaces is greatly altered by heating, owing to the formation of the granular film of oxides, it is of interest to determine how the different metallic constants as known for the polished metallic surfaces change, owing to the formation of the structure upon the surface. To a very large

extent, at least in the case of the thicker films these constants would be mainly determined by the optical properties of the film itself and only in a minor degree by the properties of the pure metal surface below, so that the changes in the optical constants may be regarded as indicative mainly of the properties of the surface structure.

The constants were determined by Drude's¹ method from the analysis of the elliptically polarised light formed when plane polarised light is reflected from these surfaces, by means of a Babinet compensator. As in case of the observations recorded in the previous sections, the constants were determined for three different wave lengths, in the red, yellow and indigo part of the spectrum by employing suitable monochromators. As a general rule, it is found that as the nature of the surface-structure changes with heating the apparent index of refraction goes on decreasing whereas the apparent coefficient of absorption k goes on increasing thus giving a consequent increase in reflecting power R of the plates. This was the case with all three wave lengths employed by the author.

The procedure adopted for the experimental determination of the metallic constants is that given in text books on optics. The results were, calculated from the following formulæ of Drude.²

$$(1) \quad k = \tan 2\bar{\psi}$$

where $\bar{\psi}$ = principal azimuth of the analyser

$$(2) \quad n = \frac{\sin \bar{\phi} \tan \bar{\phi}}{\sqrt{1 + k^2}}$$

where n = refractive Index of the medium

$\bar{\phi}$ = principal angle of incidence

$$(3) \quad R = \frac{n^2(1 + k^2) - 2n}{n^2(1 + k^2) + 2n}$$

The results of calculation are entered in the form of a table (Table III). In column 6 of this table the quantity γ has been entered. It is simply the product of the quantity (ka) explained before, with the refractive index of the scattering particles with respect to that of the pure metal surface in which they are embedded. As this quantity γ will be required in the theoretical

¹ Drude—*Ann. der. Physik.* XXXIX (1889)

² Drude—*Theory of Optics*, pages 363–364. edition 1913

calculations that follow it has been thought advisable to calculate and record it here. The value of the refractive index for the pure metal required in this transformation of (ka) to γ is taken in comparison with the values obtained by Minor.¹

IV—PHYSICAL THEORY OF SCATTERING BY CONDUCTING PARTICLES

A solution of the problem of the scattering of electromagnetic waves by a spherical obstacle has been given by Love.² Lord Rayleigh³ has shown that Love's results admit of considerable simplification and has used the simplified forms to calculate the polarisation of the scattered wave when light is incident upon a transparent sphere of refractive index 1.5 and of dimensions comparable with the wave length of light. In the present investigation similar calculations have been made for conducting spheres of copper and iron, the incident beam being a monochromatic wave of length given by $\lambda=5830 \text{ A.U.}$

Let a beam of unpolarised light travelling along the negative direction of axis of Z be incident on a spherical obstacle placed with its centre at the origin. Suppose that the observation on the scattered light are made in the XZ plane at a distance r from the obstacle.

If X , Y , Z be the electric forces parallel to the three axes in the scattered wave then the vertical and horizontal components of intensity in the scattered light are given by the squares of modulus of the complex quantities Y and

$$\frac{xZ - zX}{r}$$

According to Rayleigh⁴ we get for these two quantities from Love's solution the two following series —

$$Y = \sum_{n=1}^{\infty} (-1)^{n+1} \cdot \frac{2n+1}{n(n+1)} \left[M_n \{ \mu P'_n - n(n+1)P_n \} + N_n P'_n \right] e^{ik(ct-r)} \quad \dots (1)$$

¹ Minor—Ann. d. Physik, 4 Folge Bd X, page 617 (1903).

² Love—Lond Math. Soc Proc Vol XXX, p 308 (1899).

³ Rayleigh—Proc. Roy Soc Vol LXXIV, pp. 25-46 (1910).

⁴ Rayleigh—Loc. cit.

$$\frac{\pi Z - 1X}{r} = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} \left[N_n \{ \mu P'_n - n(n+1)P_n \} + M_n P'_n \right] \times \frac{e^{ih(ct-r)}}{kr} \quad (2)$$

In these equations $k=2\pi/\lambda$ where λ is the wave length of the incident light, $\mu=\cos \theta$ and P_n or $P_n(\mu)$ is a zonal harmonic of degree n whose axis is the axis Z . M_n and N_n are functions of the size and optical properties of the spherical obstacles. And they are given by

$$N_n = \frac{K \cdot \psi_{n-1}(ka) - \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(\eta)}{\psi_n(\eta)} \right\} \psi_n(ka)}{-KE_{n-1}(ka) + \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(\eta)}{\psi_n(\eta)} \right\} E_n(ka)} \quad (3)$$

and

$$M_n = \frac{\psi_{n-1}(ka) - \frac{\psi_{n-1}(\eta)}{\psi_n(\eta)} \psi_n(ka)}{-E_{n-1}(ka) + \frac{\psi_{n-1}(\eta)}{\psi_n(\eta)} E_n(ka)} \quad (4)$$

where K =dielectric constant of the material of the sphere

$$\psi_n(ka) = (-1)^n \cdot \frac{1}{3} \cdot \frac{1}{5} \cdots \frac{1}{2n+1} \left\{ \frac{1}{(ka)} \frac{d}{d(ka)} \right\}^n \frac{\sin(ka)}{(ka)}$$

$$E_n(ka) = (-1)^n \cdot \frac{1}{3} \cdot \frac{1}{5} \cdots \frac{1}{2n+1} \left\{ \frac{1}{(ka)} \frac{d}{d(ka)} \right\}^n \frac{e^{-ika}}{(ka)}$$

and a =radius of the spherical obstacle.

$\eta=m(ka)$, where m is the refractive index of the material of the sphere with respect to the surrounding medium

There is however a further relationship between the functions E_n and ψ_n . Because ψ_n is the imaginary part of the complex function E_n . So that separating the real and imaginary parts

$$E_n(\eta) = \Psi_n(\eta) - i \psi_n(\eta) \quad (5)$$

Relations similar to (1) and (2) above have been used by Mie¹ to calculate the intensity and polarisation of the light scattered by small gold particles. And it is to be noted that Mie's solution of the problem of the scattering of light by a sphere is identical with Love's, though obtained independently and expressed rather in a different manner

Hence, to arrive at the expressions for M_n and N_n for a per-

¹ Mie—Ann. d. Physik, 4 Folge, Bd XXV, p. 487 (1908).

fect conductor we may make use of the expressions given by Sir J. J. Thomson in his "Recent researches in electricity and magnetism," page 446, as has been done by Talbot-Paris.¹ The expressions given by J. J. Thomson as referred to above, give the electric forces in the waves scattered by a sphere having the character of a perfect conductor. But these expressions can be utilised only in the case of ordinary conducting metals provided that the distance which the alternating currents generated by the incident vibrations, penetrate into the sphere, is small compared with the diameter of the sphere. This condition, however, cannot be fulfilled by any known metal when we are dealing with oscillations of the frequency of light and can only be expected to be fulfilled in the case of incident Hertzian waves on the spheres of metals like copper.

By making proper alterations in the notations used by Thomson for the electric forces in the scattered wave we get expressions identical with those of Love, the only difference being in the expressions for M_n and N_n . According to J. J. Thomson, for a perfect conductor

$$M_n = -\frac{1}{(ka)^n} \frac{S_n(ka)}{f_n(ka)}$$

and

$$N_n = -\frac{1}{(ka)^n} \cdot \frac{\frac{d}{da} \left\{ a S_n(ka) \right\}}{\frac{d}{da} \left\{ a^{n+1} f_n(ka) \right\}}$$

where, as before $k=2\pi/\lambda$ and a =radius of the sphere moreover,

$$S_n(ka) = (ka)^n \left\{ \frac{1}{ka} \frac{d}{d(ka)} \right\}^n \cdot \frac{S_n(ka)}{(ka)}$$

and

$$f_n(ka) = \left(\frac{1}{ka} \cdot \frac{d}{d(ka)} \right)^n \cdot \frac{e^{-ika}}{(ka)}$$

Hence for the expressions M_n and N_n in terms of E_n and ψ as before, we have,

$$M_n = \frac{\psi_n(\eta)}{-E_n(\eta)} \quad \dots \dots \dots (6)$$

¹ Talbot-Paris—Phil. Mag. Vol. 30, Oct 1915

and

$$N_n = \frac{(2n+1)\psi_{n-1}(\eta) - n\psi_n(\eta)}{-(2n+1)E_{n-1}(\eta) + nE_n(\eta)} \quad \dots \quad (7)$$

Hence M_n and N_n can easily be calculated and substituted in the equations (1) and (2) before. Since Y and $\frac{xZ-zX}{r}$ are both complex quantities we may put

$$Y = Y_1 + i Y_2$$

$$\frac{xZ-zX}{r} = Z_1 + i Z_2$$

So that
$$\frac{\text{vertical component of intensity}}{\text{horizontal component of intensity}} = \frac{Y_1^2 + Y_2^2}{Z_1^2 + Z_2^2}$$

This relation can easily be determined experimentally and truth of the assumptions will thereby be established.

V—THEORETICAL RESULTS FOR COPPER AND IRON PLATES.

In order to calculate the polarisation curves for light scattered by small particles, it is necessary to make use of the general expressions for M_n and N_n already quoted (page 31). In taking in value for η however, the refractive index of metallic copper and of the surface-structure formed by heating are both to be considered. Hence the values of η calculated in the Table III are taken.

The first step towards obtaining the values of M_n and N_n is to calculate the value for $\psi_n(\eta)$ from the series.

$$\psi_n(\eta) = 1 - \frac{\eta^2}{2 \cdot 2n+3} + \frac{\eta^4}{2 \cdot 4 \cdot 2n+3} - \frac{\eta^6}{2n+5} \dots$$

Hence, to obtain the values for $\psi_n(\eta)$ for moderate values of n the sequence equation

$$-\frac{\eta^2}{2n+3} \cdot \psi_{n+1}(\eta) = (2n+1) \left\{ \psi_{n-1}(\eta) - \psi_n(\eta) \right\}$$

is employed.

The values of $E_n(\eta)$ are calculated from relations¹

$$E_0(\eta) = \frac{e^{-i\eta}}{\eta}$$

and

$$E_1(\eta) = 3 \cdot \frac{1+i\eta}{\eta^2} e^{-i\eta}.$$

¹ Rayleigh—Loc. cit.

and the sequence equation

$$E_{n+1}(\eta) = \frac{(2n+1)(2n+3)}{\eta^2} \{ E_n(\eta) - E_{n-1}(\eta) \}$$

Hence since $E_n(\eta) = \Psi_n(\eta) - \psi_n(\eta)$ the value of both the functions Ψ_n and ψ_n are known. The following table (Table IV) will give the values of these two functions. The values are checked as far as practicable. Next, with the values for Ψ_n and ψ_n and with the help of the relations deduced before, the Table V giving the values for M_n and N_n is made.

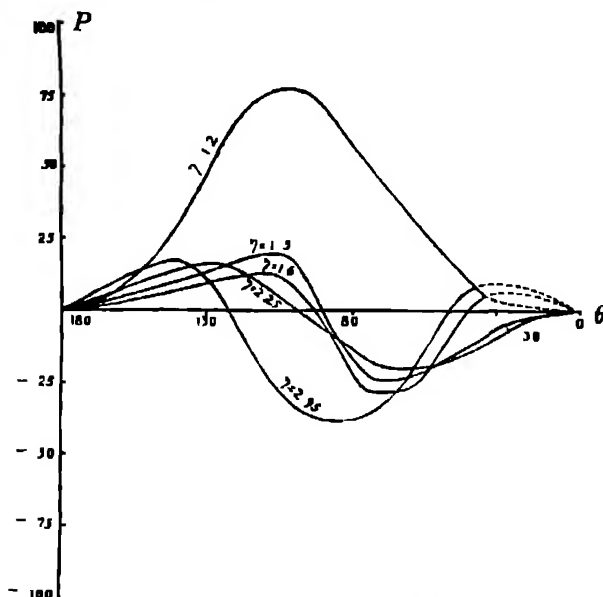


FIG. 3 Theoretical curves for Copper and Iron.

The logarithmic values of

$$\frac{(2n+1)P'_n}{n(n+1)} \quad \text{and} \quad \left\{ \frac{(2n+1)\mu P'_n}{n(n+1)} - (2n+1)P_n \right\}$$

have been tabulated by Rayleigh¹ for the five values of μ , viz. $\mu=0, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ and 1. Thus the expressions for the vertical and horizontal components of the electrical force in the scattered waves may be calculated for different directions given by the values of $\mu=\cos \theta$. When μ is negative $\frac{(2n+1)P'_n}{n(n+1)}$ changes sign if n is even and the other quantity changes sign if n is odd. Hence the values

¹ Rayleigh—Loc. cit.

for the squares of the moduli are calculated for five different values of η and the value of P obtained in these cases also. The results are entered into a table (Table VI).

The values of P are plotted against the corresponding values of θ (Fig. 3) making use of the same units as in the case of Figs. 1 and 2.

In comparing the two sets of curves, one obtained experimentally, (Figs 1 and 2), and the other calculated from the theory (Fig. 3), it will be found that for the smallest size of particle, viz $\eta=1.2$, the two curves are almost similar, there being a direction of maximum polarisation between $\theta=100^\circ$ to 90° . In the curve for $\eta=1.6$ the position of the neutral point is almost the same. But the value for maximum value of P both on the negative and on the positive sides of the axis is greater in the case of the theoretical curve than in the experimental curves. The error may be due to the estimation of the intensity—equalisation in those positions. There are such discrepancies in case of the other curves which lie within the limit of experimental error and on the whole the two sets of curves may be considered identical. The calculations in case of such large particles as given by $\eta=6.4$ was not tried on account of the tediousness of the task and the larger calculation that it will involve. For, the calculations in case of the smaller particles were made easy by the calculated results of Rayleigh for the factors which finally multiply M_{\parallel} and N_{\parallel} . Thus, the theoretical calculations were restricted only to five cases. Thus the phenomena observed and recorded in the preceding pages may be accounted for by considering the cause as the scattering of light by the close-grained discontinuous structure formed upon the polished metallic surface in the process of heating beyond the tempering range. As the scattered light is distributed over quite a wide range its colour changing continually, we should expect to find the scattered light in the directions in which it is brightest to be complementary to the reflected light. To account for the non-changeability of the colour as the tempered surface is gently polished, the argument may be put forward that since the small particles playing the whole part are of dimensions small compared with the wavelength of light, they will be removed from the surface wholly and never in parts, however gentle the touch of the polishing apparatus may be. Thus by polishing

gently, we simply reduce the number of particles distributed over the area, which is the cause for falling off in intensity of the light observed by Mallock. Moreover, this conception of granular structure and the scattering by the small particle fits in closely with the phenomena of periodic recurrence of colours observed both in case of copper and iron.

That the time of heating plays a part in these cases, there is no doubt. But the fact that the second stage of re-appearance of colours could not be obtained unless the end of the copper plate was put in contact with the Bunsen flame itself cannot be ignored. As a sort of explanation it may be put forward that as heat is applied to the plate, the molecules lying at random (the idea of Beilby) are not affected all at once. If the temperature is kept constant, more and more molecules will be caused to take part in the process and some will form aggregates forming bigger particles which account for the gradual change in colour. That the colours may be obtained even at quite a low temperature (100°C) may be seen on looking at the inner surface of the double-walled copper-made water-baths used so often for keeping a thing at a constant temperature. If the surfaces are sufficiently clean and polished, almost all the colours will be found there in quite a beautiful manner. The author of the present paper however, put a polished copperplate inside one of such water-baths. After an operation for about a month, the water being heated for about five hours daily, a violet tint was obtained upon the plate. That longer exposures will bring in other colours is quite apparent from the colours upon the body of the water-bath itself. But here the metal is being heated in contact with the water vapour and hence the re-action taking place in the formation of aggregates is of quite a different nature from that under investigation.

Again, by this slow heating the degree and nature of oxidation of the molecules will also go on changing so much so that on continuation of heating at the same temperature which is rather low, the particles instead of forming into still larger aggregates necessary for the colours in the second stage, will gradually pass on to form the black-oxide. Hence it was that the high temperature of a Bunsen flame was necessary to form larger aggregates long before the nature of the particles was changed to the complete oxidation stage.

VII.—SUMMARY AND CONCLUSION.

(1) In the present paper an attempt has been made to explain the colours exhibited by tempered steel and other tarnished metal surfaces, the diffraction of light by the granular film of oxide formed during tempering playing the main part in the theory on the lines first suggested by C. V. Raman.

(2) The experiments made with differently heated plates of different metals supply strong evidence that the colours are due to the granules.

(3) The experiments done consist in—

(i) Observation and study of the reflected light as the angle of observations are changed and also of the scattered light in general

(ii) Study, in detail of the scattered light, for various angles between $\theta=0$ to $\theta=180^\circ$ with quite a large angle of incidence.

(4) Curves are drawn showing the intensity relations of the vertical and the horizontal components in the scattered light for values of θ ranging between 0° to 180° .

(5) The physical theory of scattering as developed by Love and Rayleigh has been employed with slight modifications for conducting particles as has been done by Talbot-Paris.¹

(6) The theoretical intensity curves are drawn employing different values for the size of the scattering particles which is determined by the microscopic study of the structure formed upon the metal plates

It is found that the curves obtained experimentally and from theory agree quite remarkably.

Thus the idea that the scattering of light by the surface structure is an essential part of the phenomena is supported by the detailed observations that have been made and recorded in course of this paper. The theory also explains in a general way the facts in connection with the problem known before and observed by others.

The author wishes to record his cordial thanks to Prof. C V. Raman for his great interest in the work and for providing all facilities for work at the Palit Research Laboratory.

¹ Talbot Paris—*loc. cit.*

VIII.—EXPLANATION OF THE PHOTOGRAPH.

The photograph shows the colours in different plates of iron that have been employed in the present investigation. The last figure shows the recurrence of colours on the same plate while the other plates exhibit the colour for heating for different periods as recorded in Table I.

University College of Science,
Calcutta
3rd May, 1922

TABLE I

Metal plate	Dimensions of the plate in sq. cm.	Time for which the current was switched on	Colour exhibited	Original weight of the plates in gm.	Gain in weight after heating (in gms.)	Size of the particles (μ)
<i>Copper.</i>						
I	6.2 x 3.5	1½ min.	Red tint	16.303	0.0002	1.21
II	6.1 x 3.8	2 min. 30 sec.	Violet	15.470	0.0008	1.33
III	6.8 x 4.0	2 min. 40 sec.	Green tint	15.262	0.001	1.64
IV	6 x 3.7	3 min.	Green	15.9458	0.0031	2.4
V	6.8 x 4	3½ min.	Yellow	15.562	0.006	3.196
<i>Iron</i>						
I	7 x 4	3 min.	Indigo tint	24.9412	0.0008	1.423
II	6.8 x 4	3½ min.	Indigo	25.591	0.001	1.691
III	6.9 x 3.8	5 min.	Blue	23.568	0.004	3.054
IV	6.9 x 4.6	10 min.	Green (yellowish)	28.271	0.007	4.115

TABLE II.

°	COPPER PLATE I	
	Vertical Component	Horizontal Component
160°	Greenish yellow	Bluish green
150	Yellow	Green
140	"	"
130	"	"
120	Reddish yellow	Yellowish green
110	"	"
100	Yellow	Green
90	"	"
80	Greenish yellow	"
70	"	"
60	"	"

°	COPPER PLATE II	
	Vertical Component	Horizontal Component
160	Greenish yellow	Greenish yellow
150	"	"
140	Reddish yellow	"
130	"	"
120	"	"
110	Yellowish red	Yellowish green
100	"	"
90	"	"
80	Reddish yellow	Green
70	"	"
60	"	"

°	COPPER PLATE III.	
	Vertical Component	Horizontal Component
160	Greenish yellow	Red
150	"	"
140	"	Reddish yellow
130	"	"
120	Yellowish green	"
110	"	"
100	Yellow	Yellow
90	Greenish yellow	Reddish yellow
80	"	"
70	"	"
60	"	Yellowish red

°	COPPER PLATE IV.	
	Vertical Component	Horizontal Component
160	Yellow	Red
150	"	"
140	Greenish yellow	Yellowish red
130	"	"
120	Yellowish green	Reddish yellow
110	"	"
100	"	"
90	Green	Yellow
80	Yellowish green	Reddish yellow
70	Yellow	"
60	"	Red

°	COPPER PLATE V	
	Vertical Component	Horizontal Component
160	Reddish yellow	Bluish green
150	"	"
140	Greenish yellow	Blue
130	"	"
120	"	"
110	Yellow	Yellowish green
100	"	Blue
90	Reddish yellow	Greenish yellow
80	"	Green
70	"	"
60	"	"

TABLE II—*contd.*

°	IRON PLATE I	
	Vertical Component	Horizontal Component
160	Yellow	Greenish yellow
150	"	Green
140	"	"
130	"	"
120	Greenish yellow	Yellowish green
110	"	"
100	"	"
90	"	"
80	"	"
70	"	"
60	"	"

°	IRON PLATE III	
	Vertical Component	Horizontal Component
160	Yellow	Yellow
150	Greenish yellow	Reddish yellow
140	"	"
130	"	"
120	"	"
110	"	"
100	Yellow	"
90	"	Yellow
80	Greenish yellow	Reddish yellow
70	"	"
60	"	"

°	IRON PLATE II	
	Vertical Component	Horizontal Component
160	Yellow	Yellow
150	"	"
140	"	Green
130	"	"
120	Greenish yellow	Yellowish green
110	"	Green
100	"	"
90	"	"
80	"	"
70	"	"
60	"	"

°	IRON PLATE IV	
	Vertical Component	Horizontal Component
160	Reddish yellow	Greenish yellow
150	"	"
140	Yellow	"
130	Greenish yellow	Reddish yellow
120	"	"
110	"	"
100	Yellow	" Yellow
90	"	"
80	Greenish yellow	Reddish yellow
70	"	"
60	"	"

TABLE III.

Metal plate	$\lambda \times 10^3$ cm.	n (Refractive index)	k =Co-efficient of absorption.	R (Reflecting power)	$n=m(\lambda a)$ where $m=\frac{n}{n'}$	n' =refractive index of the polished surface
Copper-plate I	6290 5830 4380	0.571 0.644 1.098	4.705 4.0111 2.050	75%	1.2	0.650
Copper-plate II.	6290 5830 4380	0.562 0.637 1.08	5.670 4.718 2.246	78.6%	1.3	
Copper-plate III	6290 5830 4380	0.552 0.620 1.075	7.115 5.673 2.475	86.9%	1.57	
Copper-plate IV	6290 5830 4380	0.500 0.608 1.07	9.514 7.125 2.605	91.5%	2.25	
Copper-plate V	6290 5830 4380	0.496 0.600 1.060	14.300 9.534 2.747	96%	2.95	
Iron plate I	6290 5830 4380	1.727 2.352 2.527	1.664 1.483 1.428	50%	1.35	2.480
Iron plate II	6290 5830 4380	1.661 2.346 2.422	1.732 1.600 1.428	53.7%	1.5	
Iron plate III	6290 5830 4380	1.552 2.132 2.363	1.732 1.732 1.588	54%	2.625	
Iron plate IV	6290 5830 4380	1.480 1.748 2.132	1.881 2.104 1.732	54.5%	2.90	

TABLE IV

$\eta=1.2$ (COPPER PLATE)			$\eta=1.5$ (COPPER PLATE)		
n	Ψ_n	ψ_n	n	Ψ_n	ψ_n
0	30205	0.77650	0	04716	0.66499
1	2.57051	0.86298	1	1.3920	0.79235
2	23.630	0.90092	2	8.9713	0.84900
3	510.85	0.92232	3	117.89	0.88121
4	21315	0.93608	4	3049.3	0.90204
5	—	0.94592	5	—	0.91664
6	—	0.97695	6	—	0.92743

$\eta=2.95$		
n	Ψ_n	ψ_n
0	— 33550	0.06462
1	— 04892	0.36070
2	+ 61520	0.51039
3	+ 2.6707	0.60318
4	14.876	0.66456
5	138.81	0.70985
6	2035.5	0.74416

$\eta=1.6$			$\eta=2.25$		
n	Ψ_n	ψ_n	n	Ψ_n	ψ_n
0	— 01798	0.61702	0	— 27918	0.34581
1	+ 1.17906	0.75697	1	+ 29563	0.57717
2	70.141	0.82029	2	1.70318	0.68552
3	942.76	0.86578	3	9.73119	0.74909
4	21459	0.88920	4	99.904	0.79107
5	—	0.90563	5	1933.5	0.82092
6	—	0.91781	6	51793.7	0.84327

TABLE V

n	M_n	N_n
$\eta = 1.2$		
1	-0.30172-1 x 10128	0.49602-1 x 29812
2	-0.03807-1 x 00145	0.09536-1 x 010126
3	-0.00181-	0.00259-
$\eta = 1.5$		
1	-42994-1 x 24458	0.49944-1 x 39935
2	-09877-1 x 009768	0.22756-1 x 05466
3	-00746-1 x —	0.01134-1 x 000128
4	-000296-	0.00038
$\eta = 1.6$		
1	-45484-1 x 29201	0.49545-1 x 56793
2	-01169-1 x 000136	0.01596-1 x 00025
3	-000916	0.00116
$\eta = 2.25$		
1	-40579-1 x 07921	40044-1 x 14169
2	-34645-1 x 13948	48574-1 x 38161
3	-07652-1 x 00589	16066-1 x 02066
4	-00791-1 x —	00676-1 x 000045
5	-000424	00053
$\eta = 2.95$		
1	+13320-1 x 98212	-016908-1 x 002944
2	-49182-1 x 40798	+41619 -1 x 22085
3	-21455-1 x 04831	+38833 -1 x 18510
4	-04446-1 x 001986	07787 -1 x 00606
5	-00511-1 x 000026	00709 -1 x 00005
6	-000363	000437

TABLE VI.

$\mu = \cos \theta$ 1 $\frac{3}{4}$ $\frac{1}{2}$ $\frac{1}{4}$ 0 $-\frac{1}{4}$ $-\frac{1}{2}$ $-\frac{3}{4}$ -1	$\eta = 1.2$			$\eta = 1.5$		
	$Y_1^2 + Y_2^2$ (I_1)	$Z_1^2 + Z_2^2$ (I_2)	P	$Y_1^2 + Y_2^2$	$Z_1^2 + Z_2^2$	P
	0.8461 1.716 1.194 0.8486 0.6206 0.3328 0.4405 0.3895 0.5855	0.8461 1.2705 0.5963 0.2142 0.0777 0.0598 0.1082 0.2067 0.5855	0 14.92 33.01 59.84 77.73 69.53 60.54 29.71 0	0.9287 0.6595 0.9040 1.1276 1.3011 1.3079 1.407 1.4378 2.461	0.9287 0.8146 1.313 1.4403 1.5110 1.237 0.9381 1.0604 2.461	0 -10.5 -18.45 -12.16 -3.70 +2.78 +20.00 +15.00 0
	$\mu = \cos \theta$		$Y_1^2 + Y_2^2$	$\eta = 2.95$		
				$Z_1^2 + Z_2^2$	P	
	1 $\frac{3}{4}$ $\frac{1}{2}$ $\frac{1}{4}$ 0 $-\frac{1}{4}$ $-\frac{1}{2}$ $-\frac{3}{4}$ -1		2.0289 2.1038 2.0203 1.7990 2.6075 3.3075 3.0610 6.2855 15.79	2.0289 1.8447 3.4832 3.7880 5.6497 5.2506 2.9980 4.3545 15.79	0 +6.5 -26.57 -35.57 -36.84 -35.61 +7.29 +18.13 0	
	$\eta = 1.6$			$\eta = 2.25$		
	$Y_1^2 + Y_2^2$	$Z_1^2 + Z_2^2$	P	$Y_1^2 + Y_2^2$	$Z_1^2 + Z_2^2$	P
	1.0237 0.687 1.1389 0.8618 0.9092 1.2927 1.288 1.981 2.659	1.0237 0.808 1.381 1.4137 1.0986 0.8122 1.0239 1.562 2.659	0 -7.09 -9.5 -22.80 -9.4 +21.78 +15.5 +12.2 0	1.2095 4.3414 1.0658 6.429 1.3333 0.8268 1.8043 2.1407 6.3199	1.2095 3.9872 1.7811 0.7625 1.4000 0.6010 1.2048 1.7860 6.3199	0 +4.253 -18.6 -8.4 -2.4 +15.8 +19.9 +8.5 0

XI. Thunderstorms in Trivandrum.

By K. R. Ramanathan, M.A., Director of the Trivandrum Observatory.

I —INTRODUCTION AND SUMMARY

Thunderstorms are a regular feature of Trivandrum weather. They present well-marked seasonal and diurnal variations. The maximum activity occurs during the months March to May and in October. In the following paper, an analysis is made of the seasonal variations of thunderstorms in Trivandrum and they are discussed together with the variations of other meteorological elements, humidity, temperature and air movement both at Trivandrum and at Augustia (6,200 ft. above sea level) in the light of Simpson's theory of thunderstorm formation. According to Simpson, whenever there are strong humid, ascending air currents in the atmosphere accompanied by condensation of moisture, splitting of water-drops and separation of electricity occur. The conditions that have been recognized as essential for the formation of strong humid ascending air currents are (1) sufficient moisture in the atmosphere and (2) a vertical temperature-gradient exceeding the adiabatic lapse-rate. So far as these two factors go, they are satisfied at Trivandrum at all the months of the year. The reason why, then, thunderstorms do not occur at all seasons is shown to be connected with the existence of strong horizontal winds at and above the level of the Western Ghats in the months June to September and November to February, and the comparative absence of such steady air movements during the rest of the year. Strong horizontal winds prevent the formation of strong ascending currents.

II.—STATISTICS OF THUNDERSTORMS

Observations of thunderstorms in Trivandrum made during the years 1856-1864 by Mr. J. A. Broun have been discussed in

the Indian Met. Memoirs Vol. X, part 1 by Sir J. Elliot. Further records have been kept in the Trivandrum observatory from 1892 onward, when they were begun by Dr A. C. Mitchell.

Table I gives the number of days on which thunder was heard in the different months of the years 1902-1914.

Table II gives the number of days on which lightning was seen with or without thunder

TABLE I. *Number of days on which thunder was heard*

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct.	Nov	Dec.	TOTAL
1902	3	1	13	28	23	10	0	0	6	16	14	8	122
1903	2	2	6	26	17	10	0	0	2	11	8	7	91
1904	2	2	9	19	13	8	4	0	0	22	9	1	89
1905	0	4	4	23	15	2	0	0	2	10	9	0	69
1906	0	5	7	14	19	3	0	3	1	20	13	8	90
1907	2	1	17	22	21	5	2	1	14	19	12	7	113
1908	7	8	14	17	12	6	1	0	1	8	7	2	83
1909	1	7	14	22	11	1	1	2	0	14	14	7	94
1910	1	6	13	18	12	5	4	3	1	11	15	0	89
1911	0	1	12	6	17	5	1	0	3	15	8	10	78
1912	1	4	7	24	22	6	0	0	3	14	10	0	101
1913	3	4	5	20	21	4	1	2	2	10	10	6	88
1914	2	3	13	19	16	8	1	2	5	14	11	7	101
Average	2	3	10	20	17	6	1	1	3	15	11	5	93

TABLE II *Number of days on which lightning was seen with or without thunder*

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	TOTAL
1902	3	2	16	29	30	14	0	2	8	22	18	11	155
1903	2	4	10	30	22	13	0	0	2	15	15	9	121
1904	2	6	14	22	23	9	4	1	2	22	9	4	117
1905	0	10	13	26	26	2	0	0	5	11	16	4	113
1906	7	3	12	15	20	5	0	7	4	22	13	10	118
1907	2	7	26	25	25	8	5	1	5	24	15	7	150
1908	9	11	17	20	15	6	2	0	4	10	7	3	104
1909	1	10	16	23	18	3	1	2	0	18	19	8	119
1910	1	6	14	19	14	11	5	3	1	14	17	0	105
1911	2	2	16	10	19	8	1	1	6	15	16	12	108
1912	2	7	10	28	23	19	1	3	10	15	16	3	142
1913	4	6	6	24	25	8	1	2	8	14	17	7	122
1914	3	4	18	22	18	9	1	2	10	21	16	9	133
Average	1	6	14	23	22	9	2	2	5	17	15	7	124

It will be observed that the maximum thunderstorm activity occurs during March to May. There is also a secondary maximum in October. The distribution of thundery weather during the year is shown graphically in Figure 1.

An examination of the records also shows that the thunderstorms begin either to the north or east of Trivandrum, except just previous to the burst of the monsoon or when depressions are

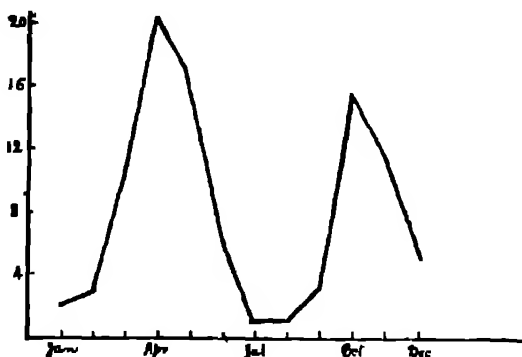


FIG 1.

travelling close to Trivandrum (when they may begin in any direction) and that they are most active during the afternoon hours 2 to 5 p.m.

III —MODE OF FORMATION.

The most satisfactory theory of thunderstorm formation is that due to Dr G C. Simpson.¹ He showed that splashing of water drops by air currents produces electrification, positive on the drops and negative in the air. When there is opportunity for a large breaking up of water drops, a large quantity of electrification is produced. In the region of humid ascending atmospheric currents, there would be condensation of moisture due to adiabatic cooling, and if the ascending currents are strong, the condensed drops would not be allowed to fall down but would be carried up until they reach a certain size and thereafter their shape would get so much out of the spherical that they would become unstable and break up into smaller drops. Dr. Lenard has shown that the limiting size of waterdrops beyond which they cannot grow without breaking up is about 5 millimetres in diameter and the limiting velocity which drops of this size would acquire on free fall is nearly equal to 8 metres per second. Hence, no drops could fall through an ascending current of air with a vertical velocity greater

than 8 metres per second. The drops would be carried up, reach a certain size, break up, and again be carried up, grow, and break up. Dr. Simpson showed that enough electricity could be produced on the drops by such splashing as would be sufficient to account for the electricity carried down by rain.

Accepting this theory, we shall see how the conditions are favourable for the formation of thunderstorms in the months of March, April and May and in October and November, and how they are unfavourable during the other months.

The conditions favouring strong ascending currents accompanied by large condensation are —

1 Enough moisture in the lower air for clouds to form as a result of upward movement,

2 A rate of fall of temperature with height approaching or exceeding the adiabatic lapse rate for saturated air, and

3 Absence of strong horizontal winds for a few kilometres above the earth's surface.

I We shall take these points one by one.

Table III gives the actual pressure of the vapour present in the atmosphere in the different months of the year at Trivandrum and at Augustia peak (Lat $8^{\circ} 37' N$, Long $77^{\circ} 30' E$, height 6,200 ft above sea level and distant 22 miles from Trivandrum, a high solitary peak in the Western Ghats where an Observatory was maintained by the Government of Travancore during the years 1856–1858 and in 1864 under the direction of Mr J. A. Broun for taking magnetic and meteorological observations)

They are taken from the Indian Met. Memoirs Vol X, parts I and II and are based on 24 hourly observations of the wet and dry bulb thermometer during the years 1856–1864 at Trivandrum and 1856–1858 at Augustia

Month	TRIVANDRUM.		AUGUSTIA (height 6,200 ft)	
	Mean vapour pressure in inches of mercury	Humidity %	Mean vapour pressure in inches of mercury	Humidity %
January	0.69	74	0.19	93
February	0.68	71	0.38	83
March	0.78	75	0.45	89
April	0.83	77	0.50	90
May	0.87	82	0.49	97

Month	TRIVANDRUM.		AUGUSTIA (height 5,200 ft.).	
	Mean vapour pressure in inches of mercury	Humidity %	Mean vapour pressure in inches of mercury	Humidity. %
June	0.82	86	0.49	98
July	0.79	86	0.48	99
August	5.79	86	0.47	97
September	0.77	83	0.46	97
October	0.79	85	0.46	97
November	0.77	83	0.44	97
December	0.68	76	0.39	94

So far as moisture is concerned, there is plenty of it in all seasons of the year. Indeed, it is doubtful whether there are many other places on earth where there is so much of moisture at all seasons of the year.

II. It is not possible to get an accurate idea of the lapse rate of temperature at Trivandrum without observations with sounding balloons. We can, however, get much useful information from a consideration of the mean temperatures at Trivandrum and Augustia during the different months of the year.

Table IV, gives the mean temperatures at Trivandrum and Augustia based on 24 hourly observations, 1856-64 at Trivandrum, and 1856-58 at Augustia.

Month.	Mean temperature at Trivandrum in °C	Mean temperature at Augustia in °C	Difference in °C
January	24.6	12.0	12.6
February	25.6	13.5	12.1
March	26.9	15.3	11.5
April	27.0	16.4	10.6
May	26.7	15.2	11.5
June	25.3	14.8	10.5
July	24.8	14.3	10.5
August	24.8	14.2	10.6
September	25.0	14.0	11.0
October	25.0	14.0	11.0
November	25.0	13.6	11.4
December	24.7	12.2	12.5

The minimum difference occurs during the months of June and July and even in those months, the lapse rate is 0.36° C per 100 metres (5,200 ft.—1,890 metres) a quantity far exceeding the adiabatic lapse rate for saturated air. According to Hann, the

temperature gradient for 100 metres for saturated air at 25° C under conditions of dynamical equilibrium to a height of 2,000 metres from sea level is 0.43° C per 100 metres (*Handbuch der Meteorologie*, page 182) We have no data as regards temperatures higher up. So far, then, as the first two conditions for ascensional movement are concerned, they are satisfied in all parts of the year The answer to the question why thunderstorms do not occur in all months of the year, will be clear when we have discussed the third condition.

IV — CHARACTER OF THE AIR MOVEMENT IN TRIVANDRUM.

The character of the air movement in Trivandrum is affected to a great extent by the close neighbourhood of the Western Ghats For about 20 miles to the east of Trivandrum, the country is undulating with hills and hollows, and beyond it, rises the Western Ghats to an average height of 5,000 ft During the months June to September, when the S W monsoon is in full swing, there is a strong steady wind from about $N\ 60^{\circ}W$ with little diurnal variation. During the months November to April, the air movement consists of land and sea-breezes The N.E. winds, that obtain during this period in the south of the Peninsula to the east of the Ghats, do not penetrate into Trivandrum, sheltered as it is, by the protecting effect of the Ghats The months May and October are months of transition.

Since the air movement at Trivandrum is largely affected by the proximity of the high Western Ghats, it is more useful to consider the air movement at a higher level where the winds would be less hampered by geographical peculiarities. For this purpose, we shall consider the air movement at Augustia. In his discussion of Augustia meteorological observations, Sir J. Eliot summarises the general character of the air movement thus :—

“The air movement at Augustia differs essentially in many respects from that prevailing at Trivandrum The peak is the highest point of the South Travancore Hills.

In the months of December, January and February, when steady and moderate strong N.E. winds obtain in the south-west of the Bay and are continued as E.N.E. winds across the districts of Tinnevely and Madura and when light local land and sea breezes obtain in the Travancore Coast districts and the neigh-

bouring sea area, the air movement at Augustia is determined by (and is a continuation of) the massive atmospheric current from the N.E. over the Bay which is strongest in the S E of the Bay and Southern India. In this season, 5% of the wind observations are of Calms, 64% of the winds are from East and 21% from N E. and only 10% from other directions. The air movement is hence remarkably steady and is on the mean of all the data, from E N E, or more exactly, N 80° E.

"Similar conditions obtain during the third period (June to Sept) The air movement at Augustia is then determined by the S W. monsoon air current over the Arabian Sea During this period, in the years 1856-58, about 4% of the observations were of Calms, 21% were winds from N W and 72% from W and hence only 3% from the remaining six points Winds are hence even steadier in this season than in the first season of the year The mean wind direction is W N.W

"The air movement during the remaining five months of the year is essentially of a transitional character During the second period comprising the months of March, April and May the mean winds in South Madras shift in direction from East in March and April to West in May, in which month, they are practically identical in direction with the mean winds in June The mean direction of the winds at Augustia during this period shift *pari passu* with the change of direction of the air movement in Southern India and the resultant is almost nil.

"The conditions in the fourth period including the months October and November are similar to those of the second period except that the transition or change is inverse to that of the second period

"The number of Calms reported is large; 16% of the wind observations received during this period in 1856-58 were of Calms, so that they were almost as numerous as during the first transitional period March to May. It is also noteworthy that Calms are more numerous in this, as in the second season, during the day than during the night and are most frequent from 11 A.M. to 4 P.M."

Summary of weather conditions at Augustia

December, January and February	Calms	5%	}
	East	64%	
	N.E	21%	
	Other directions	10%	
March, April and May	Calms	19%	}
	East	25%	
	S W	33%	
	Other directions	23%	
June to September	Calms	4%	}
	West	72%	
	N W	21%	
	Other directions	3%	
October to November	Calms	16%	}
	West	25%	
	East	32%	
	Other directions	27%	

It will be noticed that the time of maximum thunderstorm activity coincides with the time of minimum horizontal air movement at Augustia *Absence of strong horizontal winds in the higher layers is a sine que non of strong ascending currents favourable to thunderstorm development*

During the months of March and April, when the general gradient is undefined and is too weak to exercise any control over the air movement, ascending currents begin to rise with the heat of the sun and form detached cumulus heads. These cumuli grow and with the setting in of a light humid breeze from the sea in the afternoon, they grow into large masses often crowned with false cirrus, especially to the north-east of Trivandrum where the land rise is the most marked.

By about 3 P.M. the whole sky is clouded and occasional crashes of thunder are heard. This continues for varying intervals of time and is often accompanied by rain. Ordinarily, the sky clears by about 6 P.M. and a clear night follows. As the season advances, however, the thunderstorm continues at night. The general character of the weather is very similar in October.

These considerations should apply to other places where thunderstorms are seasonal. All along the west coast of India and in Ceylon, the setting in of the monsoon is preceded by a period of thunderstorm activity.

XII. An Optical Study of Free and Forced Convection from Thin Heated Wires in Air.

**By Satish Chandra Pramanik, M Sc , Research Scholar in
the Indian Association for the Cultivation of Science.**

(Plates VIII and IX)

CONTENTS

- I —Introduction
- II —Application of the Method of Striae
- III —Description of the Photographic Records
- IV —Deflection of the Rays of light by a Hot wire
- V —Summary and Conclusion

I —INTRODUCTION

The problem of convection has received much attention in recent years and an extensive literature has grown up around it, many of the papers dealing with the convective flow of heat from cylinders immersed in fluids—a case which is of importance in view of its practical application in anemometers and gas meters. A very convenient summary of the earlier literature up to the year 1916, is given in a paper by B. B. Ray,¹ which describes also his studies of the form of isothermals in air round a heated cylinder and the optical study of the general nature of convective flow. Several other communications on the subject have also subsequently appeared K. Aichi² has discussed the problem mathematically following Boussinesq and King, extending their results to the case in which η is not small [$\eta = \frac{vc}{2k}$, v , c and k being respectively the stream velocity, the specific heat and the

¹ Proceedings of the Indian Association for the Cultivation of Science, Vol VI, Part I, 1920

² Phys Math. Soc Japan Proc 2, July, 1920

thermal conductivity of the fluid]. A. H. Davis¹ has also considered the problem for similar bodies theoretically; proceeding from the point of view of the Principle of Similitude, he derived a formula—an extension of Boussinesq's solution to viscous fluids—which he has compared with experimental results of previous workers. He has shown² that "in general both for forced and free convection the hydrodynamical formulae are in very promising agreement with published data except in the case of free convection from hot thin wires." Later on he has shown that provided allowance is made for the temp. change of the properties of the fluid his formulae are substantially satisfactory. On the experimental side Dr. J. S. G. Thomas has published numerous papers.³ His method of investigation is electrical. He has studied both free and forced convection of air (and of also certain other gases) past a hot wire in a cylinder—horizontal and vertical. He has also investigated the influence of one wire on another and on a series of others and considered the bearing of the results thus obtained on anemometry and the construction of gas meters.

The present paper is continuation of Mr Roy's work, extended to thin wires and is the fruit of the suggestion of Prof C. V. Raman who has throughout guided its author and rendered him indispensable help.

II --APPLICATION OF THE METHOD OF "STRIAE"

The experimental arrangement for securing pictures depicting the flow of the air near the hot wire are very similar to those adopted in the Töpler-Schlieren method. An arc lamp *A* (Diagram 1 below) illuminated a circular aperture *H* in a metal screen in front of it and this served as a source of light. By means of a long focus achromatic lens *L* a real image of the illuminated aperture was formed on a thin mica sheet with a circular thin metal knob *K* fixed on to it, which is just sufficient to cover the image. Just behind the mica sheet was placed a telescope *T* focussed on to the middle of the hot wire *W* which lay horizontally along the axis of the optical system.

¹ Phil Mag Vol XL, 1920, Vol XLV, 1921.

² Phil Mag February, 1922

³ Phil Mag May, 1920 and Nov 1920, Feb and May, 1921, Feb. and April, 1922, and Proc Phys. Soc. Vol. XXXII, Part V, 1920

Now, any change of density of the air in the path of a ray would make the ray deviate from its natural course and it would escape the knob and enter the telescope and the image formed by it would give an idea of the disturbance on its path. So any disturbed region on the path of the rays would produce in the telescope a corresponding image. The rays from this image (inverted) after passing through the eye piece would give an erected image on a screen placed behind the telescope. This screen in our experiment, had been the ground glass (and the photographic plate *P* while giving an exposure) of a reflex hand camera *C* from which the lens system had been removed.

The wire was heated electrically, current entering and leaving the wire through copper leads *l, l* passed through capillary glass tubes which allowed the proper fixing up of the wire.



FIG 17

To prevent the outside air motion causing any disturbance in regions around the wire, the latter was put inside a wooden box *B* with perforated upper lid, and with partially open sides through which the leads protruded outside so that electrical connections were easy.

In examining the forced convection air was blown horizontally or vertically upwards across the hot wire as desired by means of a fan, to obtain a vertical draught a fan blew air into a funnel which ended in a tube bent up at right angles below the wire. In each case an approximate measure of the velocity of wind was obtained by an ordinary anemometer.

The dimensions of the wire, the values of the heating current and the wind velocity (where used) for the photographs in Plates, VIII and IX are set forth below.

EUREKA WIRES.

I *Free Convection*

Fig No	Diameter of wires	Distance between successive wires	Length along the axis.	Heating currents in amperes
1	0.054 cm	—	10 cm	1.92
2	0.054 "	2.5 cm	10 "	1.92
3	0.054 "	2.5 "	10 "	1.92
4	0.036 "	0.5 "	7.5 "	1.35
5	0.036 "	0.3 "	7.5 "	1.35
6	0.036 "	0.2 "	7.5 "	1.35
7	0.036 "	0.1 "	7.5 "	1.35
8	0.036 "	0.1 "	7.6 "	1.35

II *Forced Convection*

Fig No	Diameter of wires.	Distance between successive wires	Length along the axis	Heating current in amperes.	Velocity of wind in cm. sec
9	0.121 cm	—	20 cm	0.0	85
10	0.121 "	—	20 "	0.0	117
11	0.036 "	0.3 cm	7.5 "	1.92	49
12	0.036 "	0.2 "	7.5 "	1.92	49
13	0.036 "	0.2 "	7.5 "	1.35	64
14	0.036 "	0.1 "	7.5 "	1.92	73.5
15	0.036 "	0.3 "	7.6 "	1.35	49
16	0.036 "	0.3 "	7.6 "	1.35	40.5

III — DESCRIPTION OF THE PHOTOGRAPHIC RECORDS

In the first figure, the two streams representing the upward flow of hot air by the sides of the wire, are slightly bent towards the right, this is due to the fact that the leads to the wire becoming hot elevates the temp^t of the surrounding air which rises up and the adjacent hot stream of air is slightly attracted by it. This phenomenon is more prominent in figures 2 and 3, where the hydrodynamical attraction is very conspicuous. The fourth figure where the arrangement is the same as in figure 2, except that the wires are rather close-together shows how the two middle streams have become shortened. This process continues through the next three figures, the middle streams becoming extinct in the 7th figure where the two wires (separated by a distance of 1 mm) act as if they were one. In the fifth and the sixth figure there is a remarkable point to be noticed—that the region a little above the wires is cooler than the region higher



FIG 1



FIG 2

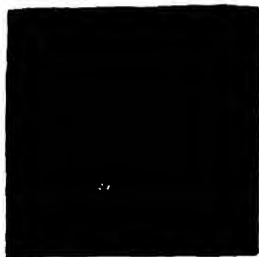


FIG 5

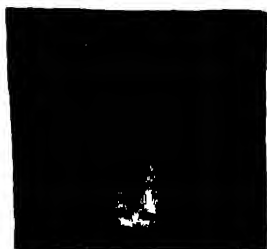


FIG 6



FIG 9



FIG 10

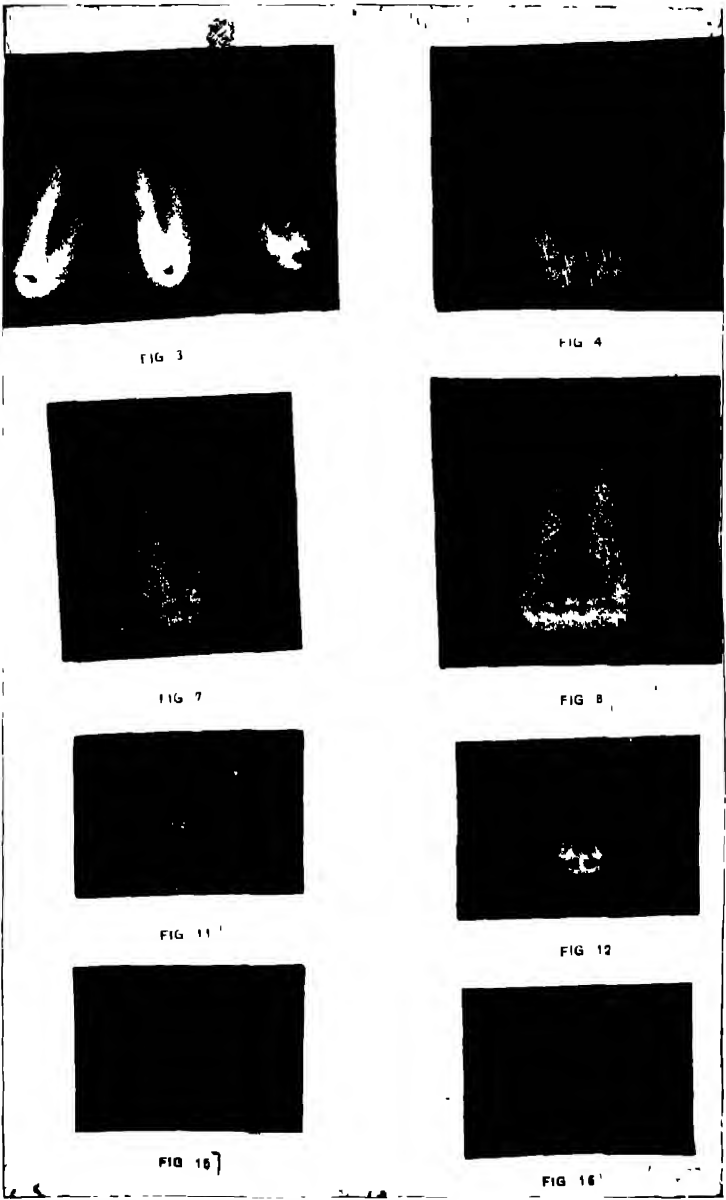


FIG 13



FIG 14

Convection from thin heated wires in air



Convection from thin heated wires in air.

up This seems to be due to the fact that the air there remains stationary ; it is too far to get much heat by conduction and too near the wires to be disturbed by convected air from surrounding regions The 8th figure shows that, for a grating of parallel wires, all the intermediate streams get annulled, the external ones having an augmented effect. Here the heat from the wires seems to be conducted, through the surrounding film, to the air below which convects it away to the external streams The grating more or less shields the air above it from any appreciable convection currents, the more effectively so the nearer the grating elements are. The above statement is true only when the velocity of the convection current is rather small.

The rest of the figures represent forced convection from hot wires The most important fact to be noticed is that there is always a thin film of hot air surrounding the wire, whether thick or thin. Besides those shown in the plate, the author has observed films in a platinum wire of diameter $\cdot 061$ mm This is no doubt due to the viscous nature of air That there exists a thin film of gas round to the hot wire had also to be postulated by Dr Thomas¹ in connection with his determination of ratio of conductivities of any two gases by the hot wire anemometer. Thus any theory of convective flow which neglects viscosity is likely to be inadequate

The first two figures of the group now under discussion, represents effect of low and high velocities in the case of single wires, the air streams being horizontal The next four figures show the effect of superimposed vertical air currents in figures 5 to 7. It will be seen that the air currents tends to make the effect of each wire independent of the others. As heat is convected away more quickly, the temp falls with a consequent diminution in the size of the streams. The last two figures correspond to the Fig 8 above in the first of them the air is blown from down upwards and in the second, from the side horizontally across the grating. In view of what has been said before, they require scarcely any special remark

Besides the facts thus far studied the author sought the effect of the proximity of a cool parallel wire near the one heated.

¹ J S. C Thomas in Phil Mag Vol 39, 1920, pp 532-34

But except a slight shortening of the streams representing a little cooling, he could optically discover no other change, though, in doing so a steady source of light was used. The eureka wire used in this connection had a diameter of .36 mm and it was heated by a current of 1.35 amperes

Dr Thomas¹ finds, in connection with experiments on forced convection from hot wires in cylindrical tubes that "if the air current be horizontal and the wires are also horizontal but perpendicular to the air current the stability of convection currents is the greatest" But while taking photographs for forced convection the author noticed that stability would be greatest if the wires are subjected to an upward transverse stream of air. The difference is no doubt due to the difference in the surroundings of the wires, in the latter case, the wires being almost in the open

IV.--DEFLECTION OF THE RAYS OF LIGHT BY A HOT WIRE.

Observation of the distribution of luminosity round the heated wire in Fig 1, Plate VIII, suggests that in its immediate neighbourhood isothermals are circular cylinders co-axial with it, the deviation from this form as we move away from the wire being much less marked below the wire than above it. The suggestion naturally arises whether it would not be possible to determine the distribution of temperature around the heated wire by a direct optical method

The first attempt in this direction was made by securing a record of the boundary and the luminosity of the image formed on the ground glass in the camera, by the deviated rays escaping a sharp knife edge placed in place of the knob. The contour lines for the various positions of the knife edge extending from the position where it just cut off the usual image of the aperture to the position where it cut off all the deviated light, were recorded on a piece of translucent paper and they were quite characteristic. But in the absence of a complete mathematical analysis connecting the shape and luminosity of the images with the position of the knife edge and the temperature distribution round the heated wire, the process could not give any tangible results.

Now, whatever might be the actual distribution of temper

¹ Phil Mag. 1920, May, pages 519-

ature round the hot wire, it is certain that the temperature diminishes as we recede from the wire. So a ray incident along the wire must get deviated upwards¹. Thus it is a priori evident that with incident light parallel and along the wire, we should get a hollow cone of rays (see Diagram 2 below) after they have traversed the disturbed region and if we put a screen just beyond the wire on it should be found a dark spot surrounded by a luminous halo.

But as the region of hot air round the wire is rather small and the temperature gradient is not insignificant, this cone of rays would, at a distance considerable compared with the thickness of the hot region, be intersected by rays that come up after traversing the cooler air distant from the wire. This would limit the minimum width of the dark spot and the boundary after this critical distance

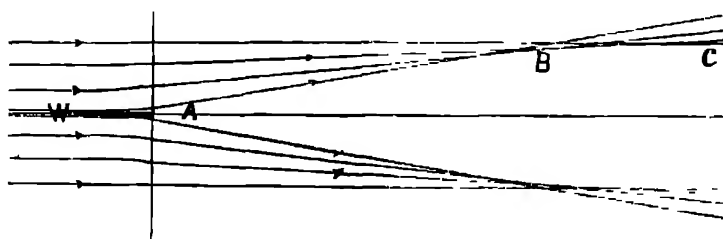


FIG 18

would be more and more hazy. Moreover the dark spot would lose its simple circular shape at a distance owing to the asymmetry produced by the two upwards hot streams of air; the effect of these streams (which are cooler than the air very near the wire) would not however be appreciable unless the dark spot is observed at a considerable distance from the end of the hot wire.

In order to test this theoretical conclusion and if possible to apply the experimental results in the determination of temperature, the source of light was brought nearer the lens so that a parallel pencil of light was incident on the disturbed region round a hot platinum wire of diameter 0.016 cm. Now, on looking through a microscope focussed near the end of the wire a circular dark spot much larger in size than that due to the obstruction of

¹ Atmospheric refraction of sound due to convective equilibrium of temperature—Rayleigh's Sound, Vol. II, Art. 288.

light by the wire itself was observed. This dark spot, though of diminished size, could be seen even at points round the wire at which the light rays had not passed over its full length. Now as the microscope was gradually moved away from the wire, the spot gradually increased in size but lost its symmetry, the effect of the upward stream of hot air presenting itself. Farther off the spot became faint over its boundary and its size reached a limiting value, the radius of the spot at such a point representing the extent to which the air below the wire gets heated.

For quantitative work, the diameter of the dark spot was measured at various distances from the wire by means of a travelling microscope. From such measurements graphs were drawn of the radius of the dark spot against the distance from the end of the hot wire. The line *ABC* in Diagram 2 indicates, though in an exaggerated way, the general form of the curves obtained, thus confirming in a general way the indications of theory. From these curves and the known values of the effect of temperature on the refractive index of air, coupled with an assumed logarithmic distribution of temp. for the regions below the hot wire, values for the temp. of the air immediately below the wire were found for various magnitudes of heating currents. The values thus obtained, though of the same order of magnitude as those found by resistance measurement were not quite satisfactory. It appears to the author that with a more exact mathematical formulation of the problem the method may prove quite successful.

Some preliminary attempts at measuring the distribution of temperature around the wire by an interference method was also made. It is hoped to repeat these at an early opportunity and to present the results in a separate paper.

V — SUMMARY AND CONCLUSION

I. After briefly reviewing recent work on the convection problem, the paper describes the results of an optical study of convective flow around hot thin wires. Three distinct methods of study are available: (a) the method of "striae," (b) the direct optical observations of the deflection of the rays of light in passing over the wire, and (c) the interference method. The results obtained by the first two methods are described.

2. The method of "striae" enables an almost exact picture of the distribution of hot air and its temperature variations as indicated by the luminosity of its various parts to be obtained. It is found that as in the case of thick cylindrical wires, so in the case of thin wires, the wire is completely enveloped by a film of hot air both in free and in forced convection, the effect presumably is the result of the viscosity of the gas. In the immediate neighbourhood of the wire the flow of heat is mainly by conduction and in the more distant parts by convection. The mutual effect of convection-currents arising from parallel heated wires, and especially the remarkable impedance offered by a parallel grating of wires for the flow of hot air through it in free convection and to a lesser extent in forced convection is illustrated by photographs.

3. These results are supported by the observations by the second method. The possibility of obtaining quantitative results is also considered.

In conclusion, my best thanks are due to Dr C. V. Raman, Palit Professor of Physics, University College of Science, who has throughout rendered the author invaluable help and put the facilities of a well-equipped laboratory at his disposal.

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5th May, 1922

XIII. On Laminar Diffraction and the Theory of Microscopic Vision.

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SYNOPSIS.

- 1 *Theory of Microscopic vision*—The mathematical theory as developed by Rayleigh, Lummer and Reiche, and Wolfke is applied in the present paper to determine the character of the images of different types of *transparent* structures under the microscope
2. *A Discontinuous Laminar Boundary*—The image of the boundary is shown to be a place of minimum intensity bordered by fine *equidistant* fringes on either side. The position of the fringes is sensibly independent of path retardation on the two sides of the boundary
- 3 *An Echelon Boundary of Two Steps*—The images of the two boundaries are places of minimum intensity compared with the other fringes bordering them. For steps of a given width, the position of maxima and minima of illumination in the field is sensibly independent of the height of the steps. The nature of the microscopic image, however, depends on the *separation* of the steps, and the diminishing clearness of resolution with their closer approach, is illustrated by three graphs
- 4 *A Laminar Transparent Ridge*.—In this case, as the ridge becomes narrower and narrower, besides the diminution in the clearness of resolution of the two edges, the entire image tends to disappear, being replaced by uniform illumination
- 5 *Experimental verification of the Results*—The results indi-

cated by theory have been tested by observations under the microscope of various actual structures (1) the striae in mica, (2) air bubbles in a thin film of liquid between two glass plates (3) fine ridges of egg-albumen formed by drying up of a 'mixed' plate, (4) fungus growths on glass, and (5) botanical and petrographical slides of various kinds. While the results of theory are broadly speaking supported by observation, a certain asymmetry in the appearance of laminar boundaries is generally observed which is not explained by the theory worked out in the paper. An explanation of the same is suggested, which, however, requires further investigation.

- 6 *Effect of Oblique Illumination*—The asymmetry referred to in (5) becomes greatly magnified under oblique illumination.
- 7 *Rayleigh's Theory of the Phenomena Observed in Foucault's Test*—The close similarity between this and the theory of microscopic vision is pointed out.

I—INTRODUCTION

The importance of the part played by diffraction in determining or modifying the character of the images of minute structures as seen through a microscope, has been widely recognised through Abbe's well-known work on the nature of microscopic images.¹ Several later writers have also dealt with the subject, notably the late Lord Rayleigh, Porter, Wolfke and others.² The published literature deals, however, mostly with the special case in which the object under observation is a grating formed of alternate transparent and opaque bars, and very little has been written about other cases, such as for instance that of laminar gratings of complex groove-form, the visibility of whose structure depends on the periodic variations of phase of the light passing through it and not upon a variation of opacity. So far as the

¹ Abbe—Die Lehre von der Bildenstehung im Mikroskop Bearbeitet und herausgegeben von O. Lummer and F. Reiche (Fr Vieweg & Sohn, Braunschweig 1910, 108 pp.)

² For references to the literature, see the paper by P. N. Ghosh *Phy. Rev.* Dec. 1919.

writer is aware, even the problem of the nature of the focussed image under the microscope of a simple laminar boundary, or of two or more parallel laminar boundaries has not been mathematically discussed. Cases of the kind above mentioned are of special interest in that the microscopic images of such structures are entirely spurious in the sense that the observed fluctuations of intensity in the field of view do not represent any actual fluctuations in the intensity of the light passing through the object. The consideration of such cases is probably quite as important as that of the simple black and white grating in interpreting the observed appearances under the microscope of various natural structures. It was with a view to fill up the gap in the literature here indicated that the writer undertook the investigation, the first instalment of the results of which are contained in the present paper. Some experimental illustrations of the mathematical theory of these cases have also been worked out.

II.—GENERAL STATEMENT OF THEORY

In their treatise on Abbe's theory, Lummer and Reiche¹ have given an expression for the amplitude of light wave at a point in the plane conjugate to the object-plane of the system. The disturbance S_2 at any point of observations in the image-plane conjugate to the point (x, y) in the object-plane is given by

$$S_2 = \frac{k}{\lambda^2} \iint_{\text{aperture}} d\xi' d\eta' \iint_{\text{object}} dXdY \phi(XY) \sin 2\pi \left[\frac{t}{T} - \psi(XY) - \frac{\xi'(x-X)}{\lambda} - \frac{\eta'(y-Y)}{\lambda} \right] \quad (1)$$

where k is a constant, λ the wave length of light, $\phi(XY)$ the transmission coefficient of the object, and $\psi(XY)$, the phase-

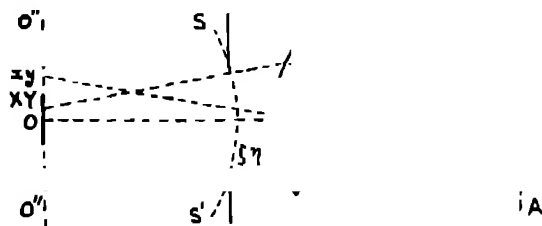


FIG. 1

change due to the object, and (ξ, η) are the coordinates of an element of ss' a sphere of radius e , described round the mid-point o of the object as shown in figure 1.

$$\xi' = \frac{\xi}{e} \text{ and } \eta' = \frac{\eta}{e}$$

are the angular height and breadth of the element. The object is illuminated by plane waves incident normally on it, so that all the diffracted rays originally start from it in the same phase. The dimensions of the object are small compared with e .

For a symmetrical object extending between the limits $-A$ and $+A$ on the x -axis and $-B$ and $+B$ on the y -axis, Wolfke¹ transforms the equation (1) to

$$S_2 = \frac{k}{\lambda} \int_{-a}^{+a} d\xi' \int_{-A}^{+A} dX \phi(X) \sin 2\pi \left[\frac{t}{\tau} - \frac{\xi'(x-X)}{\lambda} \right] \quad (2)$$

the object being supposed to introduce no phase-change, i.e. $\psi(XY)=0$, and a' is the angular height of the aperture of the objective, it being supposed to be rectangular. For a transparent object, we may $\phi(X)=1$. Further putting

$$\frac{x}{e} = \phi, \quad \frac{X}{e} = \theta, \quad \xi' = \frac{\xi}{e}, \text{ and } \pm ea' = \pm \xi,$$

the equation (2) transforms to

$$S_2 = \frac{k}{\lambda} \int_{-\xi}^{+\xi} d\xi \int_{-\theta}^{+\theta} d\theta \sin 2\pi \left[\frac{t}{\tau} - \frac{\xi(\phi-\theta)}{\lambda} \right]$$

or

$$S_2 = \frac{k}{\lambda} \int_{-\xi}^{+\xi} d\xi \int_{-\theta}^{+\theta} d\theta \sin \frac{2\pi}{\lambda} \left[Vt - \xi(\phi-\theta) \right] \quad (3)$$

where $\pm \xi$ are the limits of the aperture, and $\pm \theta$ are the angular limits of the object. Omitting the constant factor $\frac{k}{\lambda}$ for brevity, and putting $Vt=\tau$ and $\lambda=2\pi$, which can always be restored on considering 'dimensions,' we have

$$S_2 = \int_{-\xi}^{+\xi} d\xi \int_{-\theta}^{+\theta} d\theta \sin \left\{ \tau - \xi(\phi-\theta) \right\} \quad (4)$$

¹ Wolfke—*Annalen der Physik*, 34, 1911

For a transparent object introducing a constant retardation ρ , equation (2) transforms to

$$S_2 = \int_{-\xi}^{+\xi} d\xi \int_{-\theta}^{+\theta} d\theta \sin \left\{ \tau - \rho + \xi(\theta - \phi) \right\} \quad (5)$$

we now proceed to apply equation (5) to different types of laminar structures

III —CASE OF A DISCONTINUOUS LAMINAR BOUNDARY.

Let us first take the case of a transparent object, having a discontinuous laminar boundary. This, we may suppose, introduces an otherwise constant retardation ρ , which changes sign when $\theta=0$. The retardation is equal to $+\rho$, when θ is positive, and is equal to $-\rho$, when θ is negative

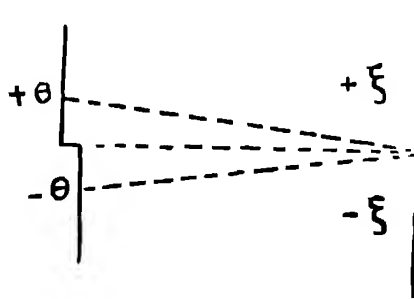


FIG 2

In this case equation (5) transforms to

$$S_2 = \int_{-\xi}^{+\xi} d\xi \left[\int_{-\theta}^0 d\theta \sin \left\{ (\tau + \rho - \xi\phi) + \xi\theta \right\} + \int_0^{\theta} \sin \left\{ (\tau - \rho - \xi\theta) + \xi\theta \right\} d\theta \right]$$

Performing the integration with respect to θ , we have

$$S_2 = \int_{-\xi}^{+\xi} d\xi \left[\frac{\sin \xi\theta}{\xi} \left\{ \sin (\tau + \rho - \xi\phi) + \sin (\tau - \rho - \xi\phi) \right\} - \frac{(1 - \cos \xi\theta)}{\xi} \left\{ \cos (\tau + \rho - \xi\phi) - \cos (\tau - \rho - \xi\phi) \right\} \right]$$

$$\begin{aligned}
&= 2 \sin \tau \left[\int_{-\xi}^{+\xi} d\xi \left\{ \cos \rho \cdot \frac{\sin \xi \theta \cos \xi \phi}{\xi} + \sin \rho \cdot \frac{(1 - \cos \xi \theta)}{\xi} \cos \xi \phi \right\} \right] \\
&- 2 \cos \tau \left[\int_{-\xi}^{+\xi} d\xi \left\{ \cos \rho \frac{\sin \xi \theta \sin \xi \phi}{\xi} + \sin \rho \frac{(1 - \cos \xi \theta)}{\xi} \sin \xi \phi \right\} \right] \\
&= \sin \tau \cos \rho \int_{-\xi}^{+\xi} d\xi \frac{\sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi}{\xi} + \sin \tau \sin \rho \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi \phi}{\xi} \\
&- \sin \tau \sin \rho \int_{-\xi}^{+\xi} d\xi \frac{\cos (\theta + \phi) \xi + \cos (\theta - \phi) \xi}{\xi} \\
&- \cos \tau \cos \rho \int_{-\xi}^{+\xi} d\xi \frac{\cos (\theta - \phi) \xi - \cos (\theta + \phi) \xi}{\xi} \\
&- \cos \tau \sin \rho \left[\int_{-\xi}^{+\xi} d\xi \frac{2 \sin (\phi \xi) - \sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi}{\xi} \right] \dots \dots (6)
\end{aligned}$$

The integrals in (6) may be expressed in terms of sine-integral and cosine-integral defined by

$$\text{si}(x) = \int_0^x \frac{\sin x}{x} dx$$

and

$$\text{ci}(x) = \int_{\infty}^x \frac{\cos x}{x} dx$$

As the aperture of the objective of the microscope is symmetrical with respect to the axis, the ci's being even functions disappear, and (6) reduces to

$$\begin{aligned}
S_2 &= 2 \sin \tau \cos \rho \int_0^{\xi} d\xi \frac{\sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi}{\xi} \\
&- 2 \cos \tau \sin \rho \int_0^{\xi} d\xi \frac{2 \sin (\phi \xi) - \sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi}{\xi} \\
&= 2 \sin \tau \cos \rho \{ \text{si} (\theta + \phi) \xi + \text{si} (\theta - \phi) \xi \} \\
&- 2 \cos \tau \sin \rho \{ 2 \text{si} (\phi \xi) - \text{si} (\theta + \phi) \xi + \text{si} (\theta - \phi) \xi \}.
\end{aligned}$$

Hence the intensity I is given by

$$I = 4 \cos^2 \rho \left\{ \text{si}(\theta + \phi)\xi + \text{si}(\theta - \phi)\xi \right\}^2 + 4 \sin^2 \rho \cdot \left\{ 2 \text{si}(\theta\xi) - \text{si}(\theta + \phi)\xi + \text{si}(\theta - \phi)\xi \right\}^2$$

The intensity at different directions ϕ , for a definite value of θ , may be easily computed by the aid of the tables calculated by Glaisher¹

In some actual observations to be described later,

$$\lambda = 5 \times 10^{-5} \text{ cm} \quad 2\xi = 20 \text{ cm} \quad \theta = \frac{\pi}{21}$$

approximately Hence $\frac{2\pi}{\lambda} \theta\xi = 598$ For facility in calculation

we may take $\theta\xi$ or rather $\frac{2\pi}{\lambda} \theta\xi = 600$ approximately We now

proceed to tabulate the values of intensity for different values of the retardation ρ When the whole difference of retardation

$2\rho = \pi$, or reckoned in wave lengths $= \frac{\lambda}{2}$, we have $\cos \rho = 0$ and $\sin \rho = 1$

It may be noted that $\theta\xi$ being 600, and the variations in the values of the si-function in the neighbourhood of $\text{si}(600)$ being very small, the expression for the intensity for values of $\phi\xi$ small compared with $\theta\xi$, reduces to

$$I = 16 \left\{ \text{si}(\phi\xi) \right\}^2 \quad (8)$$

The fluctuations of intensity with $\frac{\phi}{\theta}$ or more conveniently, with $\frac{2\pi}{\lambda} \phi\xi$ is exhibited in Fig. 3

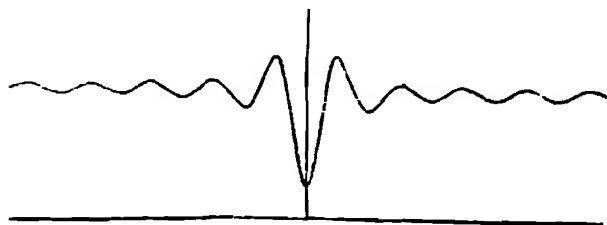


FIG. 3

The intensity is symmetrical with respect to $\phi\xi = 0$, and the fringes on either side of the central black line are equidistant

¹ J. W. L. Glaisher, Phil. Trans. 1870

Similarly for any other value of 2ρ , the variations in intensity may be calculated from (7). Only one other graph illustrating the case of $2\rho = \frac{\lambda}{3}$ has been shown

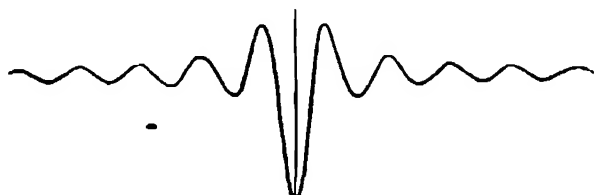


FIG. 4

We therefore conclude that the geometrical image of the lamellar boundary is always a place of minimum intensity, compared with other minimas bordering it on either side, and the positions of maxima and minima are the same for any value of ρ , except when $2\rho = \lambda$, which leads to uniform illumination in the field of view of the microscope

IV — CASE OF AN ÉCHELON-BOUNDARY OF TWO STEPS.

Next we proceed to consider the case of a transparent object with two stepped-lamellar boundaries close together as shown in Fig. 5

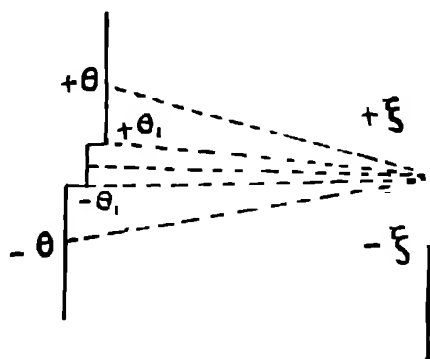


FIG. 5

The angle subtended by the boundaries at the mid-point of the aperture of the objective is $2\theta_1$. In this case, we may suppose the retardation to be constant and $= -\rho$ from $-\theta$ to $-\theta_1$,

and $+\rho$ from $+\theta_1$ to $+\theta$, and to be zero from $-\theta_1$ to $+\theta_1$, so that each step introduces a retardation of ρ_1 and the whole difference of retardation produced by the two boundaries is 2ρ

Equation (5) in this case transforms to

$$\begin{aligned}
 S_2 &= \int_{-\xi}^{+\xi} d\xi \left[\int_{-\theta}^{-\theta_1} d\theta \sin \left\{ \tau + \rho + \xi (\theta - \phi) \right\} + \int_{-\rho_1}^{+\theta_1} d\theta \sin \left\{ \tau + \xi (\theta - \rho) \right\} \right. \\
 &\quad \left. + \int_{\theta_1}^0 d\theta \sin \left\{ \tau - \rho_1 + \xi (\theta - \phi) \right\} \right] \\
 &= \int_{-\xi}^{+\xi} d\xi \left[\frac{(\sin \xi \theta - \sin \xi \theta_1)}{\xi} \left\{ \sin (\tau + \rho - \xi \phi) + \sin (\tau - \rho - \xi \phi) \right\} \right. \\
 &\quad \left. + 2 \sin (\tau - \xi \phi) \frac{\sin \xi \theta_1}{\xi} - \frac{(\cos \xi \theta - \cos \xi \theta_1)}{\xi} \left\{ \cos (\tau - \rho - \xi \phi) \right. \right. \\
 &\quad \left. \left. - \cos (\tau + \rho - \xi \phi) \right\} \right] \\
 &= \int_{-\xi}^{+\xi} d\xi \left[\frac{(\sin \xi \theta - \sin \xi \theta_1)}{\xi} (2 \sin \tau \cos \rho \cos \xi \phi - 2 \cos \tau \cos \rho \sin \xi \phi) \right. \\
 &\quad \left. + \frac{2 \sin \tau \cos \xi \phi \sin \xi \theta_1}{\xi} - \frac{2 \cos \tau \sin \xi \phi \sin \xi \theta_1}{\xi} \right. \\
 &\quad \left. - \frac{(\cos \xi \theta - \cos \xi \theta_1)}{\xi} (2 \sin \tau \sin \rho \cos \xi \phi - 2 \cos \tau \sin \rho \sin \xi \phi) \right]
 \end{aligned}$$

Omitting those terms which vanish on integration between the limits $\pm \xi$, we have

$$\begin{aligned}
 S_2 &= 2 \sin \tau \cos \rho \int_{-\xi}^{+\xi} d\xi \frac{\sin \xi \theta \cos \xi \phi}{\xi} - 2 \sin \tau \cos \rho \int_{-\xi}^{+\xi} d\xi \frac{\sin \xi \theta_1 \cos \xi \phi}{\xi} \\
 &\quad + 2 \sin \tau \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi \phi \sin \xi \theta_1}{\xi} + 2 \cos \tau \sin \rho \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi \theta \sin \xi \phi}{\xi} \\
 &\quad - 2 \cos \tau \sin \rho \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi \theta_1 \sin \xi \phi}{\xi} \\
 &= 2 \sin \tau [\cos \rho \{ \sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi - \sin (\theta_1 + \phi) \xi - \sin (\theta_1 - \phi) \xi \} \\
 &\quad + \sin (\theta_1 + \phi) \xi + \sin (\theta_1 - \phi) \xi] \\
 &\quad + 2 \cos \tau [\sin \rho \{ \sin (\theta + \phi) \xi - \sin (\theta - \phi) \xi - \sin (\theta_1 + \phi) \xi + \sin (\theta_1 - \phi) \xi \}]
 \end{aligned}$$

Let A and B denote the coefficients of $\sin \tau$ and $\cos \tau$ respectively
Then

$$I = A^2 + B^2$$

We shall now determine the nature of the diffraction pattern for $\cos \rho = 0$, i.e. when $2\rho = \frac{\lambda}{2}$ for different values of θ, ξ . The cases which present interesting features are when the two boundaries are close together, and we shall calculate the intensity pattern for different degrees of closeness

For $\cos \rho = 0$

$$I = 4 \left[\left\{ \text{si}(\theta_1 + \phi)\xi + \text{si}(\theta_1 - \phi)\xi \right\}^2 + \left\{ \text{si}(\theta_1 - \phi)\xi - \text{si}(\theta_1 + \phi)\xi \right\}^2 \right] \\ = 8 \left[\left\{ \text{si}(\theta_1 + \phi)\xi \right\}^2 + \left\{ \text{si}(\theta_1 - \phi)\xi \right\}^2 \right]$$

As before $\frac{2\pi}{\lambda} \theta_1 \xi = 600$ approximately First let $\frac{2\pi}{\lambda} \theta_1 \xi = 6$ The diffraction pattern in this case is shown in Fig 6



FIG 6

Next let $\frac{2\pi}{\lambda} \theta_1 \xi = 4$ The steps are closer than in the preceding case. Plotting the values of intensity for different values of $\phi \xi$ we get Fig 7

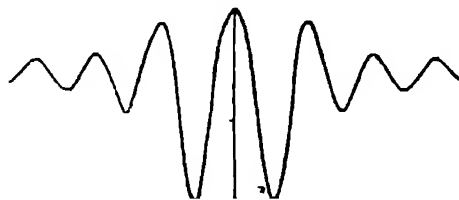


FIG 7

From Fig 6 we see that the laminar borders appear as places of minimum intensity as compared with other minimas bordering them. Between them we have some slight variations of intensity, as is shown by the presence of a dark fringe at the centre, and a bright one accompanying it. From Fig 7 we find that the images of the laminar borders are again regions of minimum intensity,

but in this case the intensity is greatest at the centre, and gradually decreases from centre to the images on either side. As we pass outwards, we meet with fluctuations of intensity gradually leading to uniform illumination. Also we conclude from the figures that the nature of the diffraction pattern between the laminar boundaries depends on the separation of the steps.

Next let $\theta_1\xi=1.6$. Here the two laminar boundaries are just resolved.

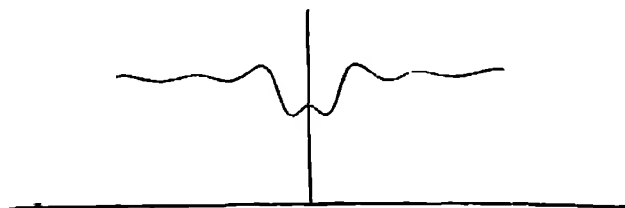


FIG. 3

Fig. 8 shows that the two boundaries are places of minimum intensity, with a brighter region between them. On either side there is the usual fluctuation of intensity rapidly ending in uniform illumination.

Lastly let $\theta_1\xi=1$. As the diffraction pattern in this case is very similar to that of Fig. 4, it has not been shown. In this case we get a region of minimum intensity along $\phi\xi=0$, and the intensity gradually increases in either direction, till we get a region of maximum intensity. The laminar boundaries cannot be located in this case, in other words, they are too close to be resolved by the microscope.

Figs. 6, 7, and 8 have been drawn for the case when $2\rho=\frac{\lambda}{2}$, but actual calculations for values of $\theta\xi=600$, $\theta_1\xi=4$, and for $\cos \rho=\frac{1}{2}$ and $\cos \rho=1$, i.e. when the total path-retardation $2\rho=\frac{\lambda}{3}$ and λ respectively, show that the positions of maxima and minima agree quite closely with those shown in Fig. 7.

Hence we may conclude as in the first case, that for definite values of $\theta\xi$ and $\theta_1\xi$, the positions of maxima and minima are the same for any value of the path-retardation, though the numerical values of intensity at the corresponding points may be different.

V —CASE OF A TRANSPARENT RIDGE.

Lastly, we proceed to consider the case of a transparent object, with two close ridges as shown in Fig 9

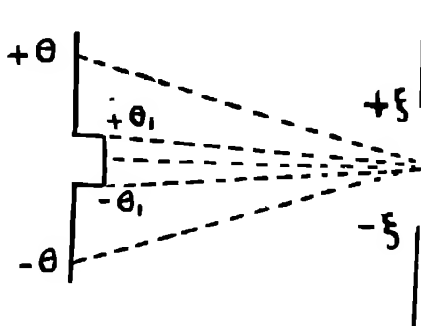


FIG 9

The angle subtended by the two ridges at o , the mid-point of the aperture of the objective is $2\theta_1$. In this particular case, the linear retardation may be taken to be constant and equal to $-\rho$ from $-\theta$ to $-\theta_1$, and $+\rho$ from $-\theta_1$ to $+\theta_1$, and again $-\rho$ from θ_1 to θ . Equation (5) then transforms to

$$\begin{aligned}
 S_1 &= \int_{-\xi}^{+\xi} d\xi \left[\int_{-\theta}^{-\theta_1} d\theta \sin \left\{ \tau + \rho + \xi(\theta - \phi) \right\} + \int_{-\theta_1}^{+\theta_1} d\theta \sin \left\{ \tau - \rho + \xi(\theta - \phi) \right\} \right. \\
 &\quad \left. + \int_{\theta_1}^{\theta} d\theta \sin \left\{ \tau + \rho + \xi(\theta - \phi) \right\} \right] \\
 &= \int_{-\xi}^{+\xi} d\xi \left[\sin(\tau + \rho - \xi\phi) \frac{(\sin \xi\theta - \sin \xi\theta_1)}{\xi} + \frac{\sin \xi\theta_1}{\xi} \sin(\tau - \rho - \xi\phi) \right] \\
 &= 2 \sin(\tau + \rho) \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi\phi \sin \xi\theta}{\xi} - 2 \cos(\tau + \rho) \int_{-\xi}^{+\xi} d\xi \frac{\sin \xi\phi \sin \xi\theta}{\xi} \\
 &\quad - 2 \sin(\tau + \rho) \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi\phi \sin \xi\theta_1}{\xi} + 2 \cos(\tau + \rho) \int_{-\xi}^{+\xi} d\xi \frac{\sin \xi\phi \sin \xi\theta_1}{\xi} \\
 &\quad + 2 \sin(\tau - \rho) \int_{-\xi}^{+\xi} d\xi \frac{\cos \xi\phi \sin \xi\theta_1}{\xi} - 2 \cos(\tau - \rho) \int_{-\xi}^{+\xi} d\xi \frac{\sin \xi\phi \sin \xi\theta_1}{\xi}
 \end{aligned}$$

Performing the integration and simplifying we have

$$S_2 = 2 \sin \tau \cos \rho \{ \text{si}(\theta + \phi)\xi + \text{si}(\theta - \phi)\xi \} + 2 \cos \tau \sin \rho \{ \text{si}(\theta + \phi)\xi + \text{si}(\theta - \phi)\xi - 2 \text{si}(\theta_1 + \phi)\xi - 2 \text{si}(\theta_1 - \phi)\xi \}$$

Let A and B denote the coefficients of $\sin \tau$ and $\cos \tau$ respectively. Then we have

$$I = A^2 + B^2$$

when

$$\cos \rho = 0, \text{ i.e. } 2\rho = \frac{\lambda}{2},$$

$$I = 4 \{ \text{si}(\theta + \phi)\xi + \text{si}(\theta - \phi)\xi - 2 \text{si}(\theta_1 + \phi)\xi - 2 \text{si}(\theta_1 - \phi)\xi \}^2$$

when $\theta\xi$ is large compared with $\phi\xi$, the expression for the intensity reduces to

$$I = 16 \{ \text{si} \theta\xi - \text{si}(\theta_1 + \phi)\xi - \text{si}(\theta_1 - \phi)\xi \}^2$$

As in the two foregoing cases, let $\frac{2\pi}{\lambda} \theta\xi = 600$ approximately. Fi-

gures 10 and 11 have been drawn for $\frac{2\pi}{\lambda} \theta_1\xi = 5$ and 4 respectively

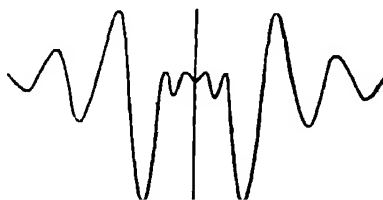


FIG 10

Fig. 10 illustrates the case for $\theta_1\xi = 5$. In this case two maxima and two minima appear between the two edges, but the latter can be distinguished by the fact that they are regions of minimum

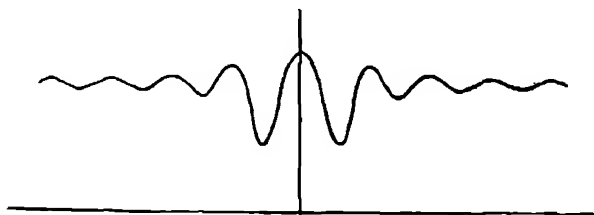


FIG 11

intensity. Outside the edges, we have as usual, fluctuations of intensity, gradually ending in uniform illumination. The maxima and minima in the region between the images are feeble in

character Fig 11 shows that in this case ($\theta_1\xi=4$), the edges are again regions of minimum intensity. But between these two regions the intensity is greatest, as distinguished from the previous case. Outside the geometrical images of the edges, we have several maxima and minima of illumination.

From these two cases, we also conclude that the diffraction pattern in the region between the images of the edges, depends on the degree of separation between them.

When $\theta_1\xi$ is small, say $=5$, the diffraction pattern is very similar in appearance to that represented in Fig 4. In the neighbourhood of $\phi\xi=0$, i.e. along the axis, the intensity is very small, it then gradually increases in either direction, the field of view being symmetrical, till we find a very bright region, accompanied by several maxima and minima of illumination. It is evident that in this case, there is nothing to indicate the geometrical images of the boundaries, i.e. they are so close together, that the microscope fails to separate them.

When the two boundaries are very close together, i.e. $\theta_1\xi$ is very small (less than 1), we find from the above expression for intensity, that it is practically constant throughout the whole field of view, since the 's1' is an odd function. In this case no image of the ridge is seen in the microscope.

The previous figures have been drawn for the case when the retardation is $2\rho=\frac{\lambda}{2}$ but calculation shows that for fixed values of $\theta\xi$ and $\theta_1\xi_1$ but for different values of $2\rho_1$ except when $2\rho=\lambda$, the diffraction pattern is similar to the corresponding cases of $2\rho=\frac{\lambda}{2}$, and the positions of maxima and minima are the same, though the absolute values of the intensity may be different.

This constant position of maxima and minima in all the three cases discussed above, furnishes us with an easy method of testing our theory experimentally.

VI.—EXPERIMENTAL TESTS OF THE THEORY

For experimental verification, several types of structure were studied. It is well known that structures occurring in nature, e.g. the cell walls and nucleus-borders of cladophora and the edges of diatoms appear as sharp black lines under the microscope. Under

direct illumination the edges can also be seen surrounded by very fine fringes in the position of accurate focus. Similar instances occur in the case of mixed plates formed of air bubbles and albumen or water.¹ For quantitative measurements, the striae in mica were used. It has been shown by P. N. Ghosh² that a stria is the boundary separating regions in the mica having slightly different thicknesses. When examined by a microscope under direct illumination, the striae appear resolved into five dark lines separated by bright regions. All the edges do not always appear equally dark, which points to the fact, that the successive steps represent unequal changes of thickness in the mica. Further the steps generally are of unequal width, and the width may vary from point to point along the length of a stria.

For the verification of the first case, a stria was chosen which showed a single edge, not resolved by a very high power Leitz objective. The source of light was a pinhole, or a slit parallel to the direction of the stria, illuminated by a powerful electric lamp, and at a sufficient distance from it, so that the mica was illuminated by plane waves incident normally on it. The edge appeared as a fine black line, accompanied by practically equidistant fringes on either side. The preceding theory shows that it is not necessary to determine the path retardation on the two sides of the stria. The microscope was fitted with a micrometer eyepiece reading up to $\frac{1}{1000}$ cm. The field of view of the mica was limited by two

Gillette razor blades fixed to it, thus forming a slit with the stria in the middle, and its edges parallel to it. It should be noted that this limitation of the field of view of mica is not sufficient to limit the aperture of the objective of the microscope, the full aperture being always effective. This was tested by the fact that the appearance of the stria, and its accompanying fringes was not changed by removing the razor blades. Thus θ could be determined, if necessary. The distance of the focal plane of the microscope from its aperture was $D=30.0$ cms and its width $2\epsilon=20.1$ cm.

From equation (8) we see that I is a minimum when

¹ C. V. Raman and B. N. Banerjee. *Phil Mag*, March 1921.

² P. N. Ghosh. *Proc Roy Soc A* Vol. 96, 1919

si $\left(\frac{2\pi}{\lambda} \phi \xi\right)$ is a minimum. From the nature of the si-function we therefore have for the first minimum value of intensity

$$\frac{2\pi}{\lambda} \phi \xi = 2\pi \text{ or } \phi = \frac{\lambda}{\xi},$$

and the successive minima are situated at intervals of 2π

Taking $\lambda = 5 \times 10^{-5}$ cm approximately, as corresponding to the brightest part of the visible spectrum, we have d the distance of the first minimum on either side from the darkest central minimum, given by

$$d = \phi D = \frac{\lambda}{\xi} D = \frac{5 \times 10^{-5} \times 300}{10} = 0.151 \text{ cm}$$

As stated previously $\frac{2\pi}{\lambda} \theta \xi$ is not required for calculation in this particular case. The following table shows the agreement to a close approximation between the observed and calculated values

$$\lambda = 5 \times 10^{-5} \text{ cm} \quad D = 300 \text{ cm} \quad 2\xi = 201 \text{ cm}.$$

Serial No	1	2	3	
Observed distance between successive minima from central one	014	013	014	cm
On the other side	013	014	015	cm

$$\text{Calculated value} = 0.15 \text{ cm}$$

The central fringe was always found to be the darkest of the system as pointed out in the theory

For the verification of the second case, such a stria was selected in the mica, which showed two steps close together, separated by a bright region. The same high power objective was used as in the previous experiment, and the angle 2θ , was determined by measuring the distance between the edges in the focal plane of the microscope by the micrometer eyepiece, and dividing it by D . The following data were obtained: $\frac{2\pi}{\lambda} \theta \xi = 630$ nearly

$\frac{2\pi}{\lambda} \theta_1 \xi = 1.08$, $D = 30.0$ cms, $2\xi = 2.01$ cm The method of illumination was the same as in the previous case.

We find from Glaisher's tables that the difference between the values of $\sin(630)$ and $\sin(600)$ is small enough to be negligible for our purpose, so for simplicity θ_2 was taken equal to 600, and $\theta_1 \xi = 1$ approximately. Fig. 7 shows the positions of maxima and minima for this case. The following table shows the agreement between the observed and calculated values —

$$\lambda = 5 \times 10^{-5} \text{ cm } \theta_1 \xi = 1, \theta_2 \xi = 600 \text{ approximately}$$

Serial No

Observed distance between successive minima (on one side)	0.145	0.145	0.160 (very faint)
On the other side	0.145	0.150	

Calculated value = 0.146 cm

The distance between the geometrical images in the focal plane was 0.195 cm and $D = 30.0$ cm

It is to be noted that it was difficult to judge the point of critical focus, and very slight changes in the position of the focus, produced appreciable errors in the measurements taken. The fringes were extremely fine, and the finite width of the moving wire of the micrometer also produced a slight error in the measurement. Considering these facts, the observed and calculated values show a close agreement.

In both these cases, the diffraction pattern showed an asymmetrical character, the fringes on one side being clearer and more in number than on the other side. This is not accounted for by the theory developed above, but nevertheless the theory explains the observed facts to a close degree of approximation.

For the third case, the boundaries studied were that of mixed plates formed of albumen and air bubbles¹. When these mixed plates are allowed to dry, the albumen forms narrow ridges, separ-

ated by broad air spaces on either side examined under the microscope, the ridges exhibited effects, which showed good qualitative agreement with the theoretical results indicated in Figs. 10 and 11. No quantitative measurements were, however, taken in this case as the exact configuration of the ridges is to some extent still uncertain.

VII—EFFECTS OF OBLIQUE ILLUMINATION.

When a single stria is focussed under the microscope, its axis being horizontal, and the light being incident normally on it, the fringes on either side bordering the sharp black image of the stria are equidistant, the only difference being noticeable is in their visibility, they, on one side, in a particular case, on the left hand portion of the field of view being more clear than on the other. As the whole microscope together with the stria is turned slowly towards the left, i.e. in the direction in which the fringes apparently appear sharp in the field of view, and its focus is kept unaltered, so that light is now incident obliquely on the stria, it is seen that the distance between the consecutive fringes on the left increases, and they become broader and diffused, whereas the fringes on the right side appear to come closer together, and become more sharp and fine. This phenomenon persists till the direction of the incident beam is very oblique.

When the whole microscope is turned gradually in the opposite direction, i.e. towards the right, the fringes on the right hand portion of the field of view of the observer, become more distant and diffused, whereas on the other side, they come closer together, and become very fine and sharp. The same changes are also noticeable in the case of a more complicated stria, consisting of more than one step, and the mixed plates mentioned above also show increased asymmetry with oblique illumination than with normal illumination.

VIII.—CONCLUDING REMARKS.

In his theory of the phenomena observed in Foucault's Test, Rayleigh¹ has investigated the distribution of intensity in the focal plane of an observing telescope, under various conditions of limit-

¹ Rayleigh, Phil. Mag., Feb., 1917.

ations of aperture of the objective, when a transparent object introducing a phase-retardation is viewed by the well-known 'knife-edge' test. The conditions involved in the theory of the method are not dissimilar to those obtaining in the theory of microscopic vision, and detailed analysis practically leads to the same results as the theory developed in the present paper. Both these theories, however, fail to explain the asymmetrical character of the effects actually exhibited in practice by laminar boundaries. The assumption that the effect of a thin laminar boundary is merely to impose a simple path-retardation on a part of the wave front is probably not quite accurate. The exact configuration of the laminar edge is undoubtedly of great importance in determining the character of the light diffracted by it through large angles. The influence of the shape of the laminar edge is particularly well-exhibited in the case of 'mixed plates,' where the edges are drawn inwards under the action of surface-tension, and a considerable amount of light is scattered at these edges.

In this connection, mention may also be made of some observations made by the writer on the effects of a certain type of fungus growth on optical glass, the edges of which exhibited the phenomena of laminar diffraction exceedingly well. The fungus shows gorgeous colours, when examined by light scattered by it in different directions, the colour depending on the angle of diffraction. When a particular edge of the fungus was singled out for observation, it showed marked asymmetry in its colours as observed from either side. The influence of this asymmetrical diffraction on the microscopic appearance of the edges remains yet to be mathematically investigated.

Another case of great importance in the theory of microscopic vision is that of laminary gratings, so far as the writer is aware, no attempt has been made to apply the rigorous theory of gratings as developed recently by Rayleigh¹ and Voigt² to the interpretation of the microscopic appearance of grating structures. The writer hopes at an early opportunity to take up this problem.

The work was carried out in the laboratory of the Indian Association for the Cultivation of Science, and the writer wishes to

¹ Rayleigh, Scientific Papers, Vol. V, pp. 388-404

² Voigt, Gottingen Nachrichten, 1910. It may be mentioned that Wulffke has dealt with the case of a simple laminary grating.

record his sense of deep gratitude to Prof. C. V. Raman for his encouragement and guidance during the progress of the work.

210, Bowbazar Street,
Calcutta, India,
5th May, 1921

XIV. On the Theory and some Applications of Sub-synchronous Pendulums.

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- I —Introduction
- II —Chronographic Determination of Frequency
- III —General Characters of Sub-synchronous Maintenance
- IV —A simple Theory of Sub synchronous Maintenance
- V.—Discussion of the Mathematical Theory
- VI —Summary and Conclusion

I —INTRODUCTION

When an iron rod swings as a pendulum over a vertical bar-electromagnet through which is caused to pass an electric current rendered intermittent by an interrupter, the pendulum is sometimes found to be maintained in a state of permanent and vigorous oscillation against the natural dissipative forces tending to bring it to rest. The magnetic force does not tend to displace the pendulum appreciably from its equilibrium position when the pendulum is at rest and so the pendulum requires an independent starting, generally with a large amplitude, from which it settles down to the amplitude requisite for maintenance

The phenomenon was noticed and investigated mathematically by the late Lord Rayleigh¹ for the case of a pendulum whose frequency was $\frac{1}{2}$ that of the interrupter. Recent work by Mr Dey and Prof C. V. Raman² has extended the limit of the frequency ratio to a wide limit, inasmuch as, the maintained oscillations of the pendulum may have a frequency which may be any one of the series of fractions $\frac{1}{2}, \frac{1}{4}, \frac{1}{6}, \frac{1}{8}$, etc., up to $\frac{1}{10}$ of the frequency of the interrupter fork and the series is capable of being

¹ Scientific Papers. Also Theory of Sound, Vol I, p. 82

² Proc Roy Soc A, Vol 95, 1919

extended to still smaller ratios for the possible frequency of maintenance. These authors have further brought out certain interesting features in the working of the sub-synchronous pendulum, namely, the variation of the amplitude of the pendulum over the possible range of frequency of maintenance, the sequence of which is totally unlike the ordinary type of resonance curve of a simple vibrator under the action of a periodic force. The paper quoted discusses the application of the pendulum to the absolute determination of acoustical frequencies and an Appendix to it contains the outline of the dynamical theory of maintenance. It is proposed in the present paper (a) to test the exactness of the numerical ratios of the frequency of the pendulum and fork-interrupter and to make by chronographic methods an accurate determination of the frequency of the fork interrupter, (b) to give a simple explanation of the fact that the maintenance occurs in even submultiple ratios of frequencies and of the other features of maintenance observed by the present writer and (c) to test by actual measurements of energy losses and gains of the pendulum on the theory of sub-synchronous maintenance given by Prof C. V Raman

The experiments described in the following pages have been done with a pendulum 35 cms long with a heavy brass bob attached to it, the suspension for the pendulum being a loop of wire working in two wire hooks. The electromagnet placed just below the pendulum rod had an iron core 12 cms. long and was fed by interrupted currents (12 amp) from a fork of frequency 32. The fork was maintained in successful oscillation for hours together by an electromagnetic arrangement, the sparking of it being smoothed by shunting a microfarad condenser across the spark gap, and submerging the mercury surface of the interrupter in a layer of absolute alcohol

II —CHRONOGRAPHIC DETERMINATION OF FREQUENCY

It has been noticed in the introduction that for the maintained oscillations of the pendulum its frequency may be any one of the series of fractions $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, etc., of the frequencies of the fork interrupter. The exact equality of the ratio of the frequency of maintenance of the pendulum to that of the interrupter fork to one or other of the fractions mentioned may be demonstrated by

various methods, and it may be shown that the pendulum follows accurately even the slight variations in the frequency of the fork, caused by fluctuations in the room temperature. This has been done by Mr. Dey in the paper quoted by three methods (i) by comparison with standard pendulum clock by visual observation of coincidences, (ii) by comparison with the ticks of a half seconds standard chronometer, (iii) by allowing the sub-synchronous pendulum to run the hands in a clock dial of which the rate can be determined against a standard time keeper

The present writer has adopted another method which is slightly more elaborate but is nevertheless easy to work and yields accurate results. The frequency of the fork is determined accurately by finding the exact time in which the sub-synchronous pendulum executes, say, one thousand oscillations, this is done with the aids of the time signals given by the pendulum on a chronograph tape at the beginning and at the end of an interval of few minutes. The seconds-pendulum of the Electric-Master-Clock in the Laboratory furnished an excellent standard being previously rated to keep time accurate to a second a day. The hammer attached to its mechanism, by half-minute impulses kept the pendulum in oscillation and the time was indicated by corresponding half-minute ticks. In order to get seconds-signals on the chronograph, an electric circuit through the pendulum rod was arranged which was completed in each swing of the pendulum by a platinum wire pinned to the bottom of the pendulum rod making contact on a mercury cup placed at the centre of swing. A similar electric circuit was arranged for records of the half periods of the sub-synchronous pendulum. The chronograph recorder supplied by the Cambridge & Paul Instrument Co, Ltd, had ink styles worked by relay circuits and the moving tape could be started and stopped by the action of a lever on the revolving gear

The experimental procedure is simply to get a few records of the pendulum and the standard clock side by side on the chronograph tape just when the clock hammer once drops, then wait for the next 22nd drop, when a few records are again taken. Thus there is a clear interval of 11 minutes between the successive records at the beginning and at the end. The chronograph gear is usually started earlier than the appointed time, so that the inter-

val between dropping of the hammer and working of the lever is practically negligible. The temperature of the fork under observation is recorded by a sensitive thermometer placed midway between the prongs of the fork. The values thus obtained of the temperature, though they might differ slightly from the actual temperature of the fork itself, have been taken to be correct, as not much deviation from the mean value was observed during a single experiment.

TABLE I

Serial number of observations	Frequency-ratio	Observed correction from record (Sec.)	Temperature of fork (degrees cent)	Calculated frequency of fork	Frequency of fork reduced to 26°C
1	$1/20$	-0.063	25.20	32.00152	31.99995
2	$1/10$	-0.211	25.46	32.00113	31.99987
3	$1/14$	-0.246	25.92	31.99998	31.99996
4	$1/12$	+0.002	26.00	31.99990	31.99990
5	$1/18$	-0.054	26.20	31.99956	31.99991

Table I shews a few results of determination of the frequency of an aluminium fork (of frequency 32 ~) while maintaining in sub-synchronous oscillation a pendulum (of length 35 cms.) It will be noticed that working with three different frequency ratios and five independent positions of the bob, it is possible to get the frequency of the fork correct to a few parts in a million.

The method of calculation was as follows—The loss or gain of the clock for an integral number of oscillations of pendulum was measured from the cross-marks on the records at the beginning and at the end. Thus the time for a complete number of oscillations of the pendulum was known. To obtain the whole number of oscillations of the fork during the interval, the loss or gain in sec. (the correction term in Table I) was divided by the rough period of the fork (0.031 sec.) and the integral part so obtained was added to or subtracted from 21, 120 (the number of oscillations of the fork in

11 min.) according as the pendulum gained on the clock or the clock gained on the pendulum ¹

III.—GENERAL CHARACTERS OF SUB-SYNCHRONOUS MAINTENANCE

With the experimental arrangements adopted, maintenance is obtained with amplitudes so large that the ordinary theory of small oscillations is not applicable. Moreover, the remarkable result is that while maintenance has been obtained at a large amplitude and the pendulum is released (e.g., by a sudden push to one side), it is not 'caught' at the amplitude at which it was maintained originally and the pendulum after executing a number of damped oscillations, is again caught at a smaller amplitude. E.g. it has been noticed that while the maintained amplitude was 49° and the pendulum made 150 oscillations in 85.1 sec. being released, it was again maintained at 35° with 150 oscillations in 82.4 sec. and then again at 10° with 150 oscillations in 80.4 sec. This point has been tested carefully with various other positions of the bob leading to the general result that maintenance is possible with two or three amplitudes when the natural frequency of the pendulum and that of the interrupter are not interfered with.

Maintenance of a pendulum in sub-synchronous oscillation is generally obtained with amplitudes ranging between 10° and 60° , with the experimental arrangements adopted, as for amplitudes less than 10° , the pendulum departs much from the plane of its motion, being often irregular apparently due to the proximity of the metal rod in vibration in the magnetic field and the consequent unavoidable generation of eddy currents in its mass. The manner in which the amplitude of the forced oscillation of the pendulum varies by varying the position of the bob in the rod so as to alter its natural period of oscillation shows the peculiarity of increasing continually to a large value as the position of the bob in the rod is raised till a stage is reached at which the pendulum

¹ Another procedure is, of course, to divide the corrected time by the period of the pendulum, determined sufficiently accurately by means of a stop watch, and multiply the integral number so obtained by the denominator in the frequency ratio, determined from a knowledge of the periods.

refuses to be maintained. This is followed by another region of maintenance, and so on.

As illustrative of the nature of variation, some results obtained by Mr Dey are quoted below.¹ The writer will have occasion to refer to them in a later section, as leading to a qualitative support of his theory.

TABLE II.

Frequency-ratio						
$\frac{1}{10}$	free period of the pendulum					
	period of the fork	19.4	19.6	19.8	20	20.1
$\frac{1}{11}$	Amplitude of forced oscillation	40°	32°	24°	18°	14°
$\frac{1}{12}$	free period of the pendulum					
	period of the fork	21.5	21.8	22		22.4
$\frac{1}{13}$	Amplitude of forced oscillation	44°	32°	24°		12°
$\frac{1}{14}$	free period of the pendulum					
	period of the fork	23.5	23.8	24		24.6
$\frac{1}{15}$	Amplitude of forced oscillation	46°	32°	24°		8°
$\frac{1}{16}$	free period of the pendulum					
	period of the fork	25.8	26	26.5		27
$\frac{1}{17}$	Amplitude of forced oscillation	40°	32°	16°		8°

Still another result of interest in the maintenance to be noted is the relation between the period of the pendulum while vibrating freely in the field of gravity and the periods of maintenance with different amplitudes. The experimental results obtained point to the fact that the free period of the pendulum is decreased by the presence of the electromagnet.

¹ The figures in Table II are roughly gathered from fig. 1, p. 536, Proc. Roy. Soc. A Vol. 95, 1919

Fig. 1 shews the free and forced periods of oscillation plotted against successive amplitudes. The free period of the pendulum at a definite amplitude was determined by taking the mean value of the time for a number of oscillations while the pendulum was executing damped oscillations about the amplitude in question.

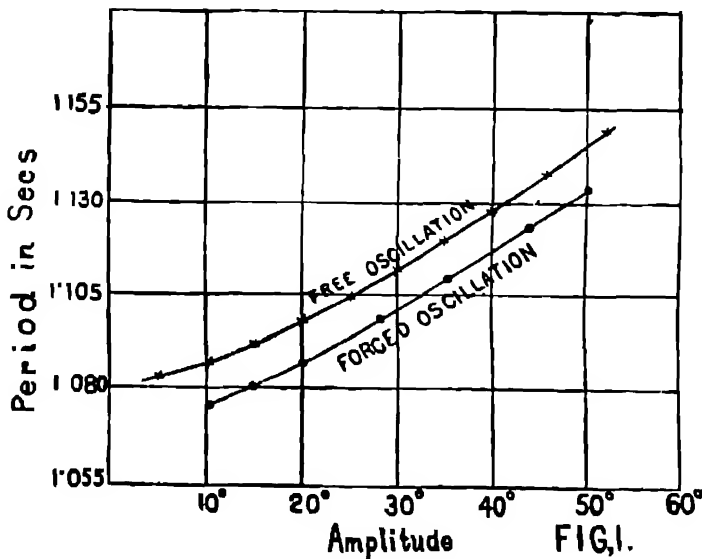


FIG. 1

The forced periods represent the periods of maintenance obtained at different amplitudes by loading the fork with small weights so as to alter its frequency. It will be noted that the free and forced periods do not differ much, a result of much theoretical significance, as will appear from the discussion of theory given later on.

Lastly, it may be remarked that the difficulty sometimes experienced in getting maintained oscillations of the sub-synchronous pendulum, is attributable to the want of exact phase relationship between the oscillations of the pendulum and that of the magnetic field. Experience shews that maintenance is most likely when the pendulum receives the least jerking when passing over the electromagnet, thus shewing that it passes its equilibrium position a little before or after the maximum phase of the field.

The actual phase difference has been studied for a number of cases, by recording on a moving photographic plate the oscilla-

tions of a steel blade by reflecting a spot of light from a small mirror fixed on to it. The blade is fixed horizontally in the neighbourhood of the electromagnet by a bifilar suspension under tension, adjusted for resonance. The pendulum while passing through its equilibrium position occults the moving spot of light. The actual phase difference can then be measured from the occultation phase,—knowing that the oscillations of the spot of light follow those of the field by quarter of an oscillation. Thus it has been found that the difference of the phases of the pendulum and the field which is almost zero for small amplitudes becomes greater and greater till it attains the value $\frac{\pi}{2}$ for very big amplitudes of maintenance.

IV.—A SIMPLE THEORY OF SUB-SYNCHRONOUS MAINTENANCE

That the behaviour of the pendulum in sub-synchronous oscillation is unlike that of a vibrating system which when acted on by a periodic force, ultimately vibrates in a period the same as that of the force, is apparent, but the analogy becomes clear and close on consideration of the fact the difference in the present case is due to the adaptability of the pendulum to the low period

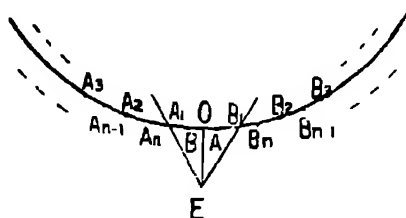


FIG. 2.

FIG. 2

of the fork interrupter limited by the range of adjustment of the period of the pendulum to the case of exact synchronism, and thus the pendulum vibrates so as to be synchronous with an even multiple of the period of the fork to which it happens to be near by reason of its own limited free period. Why the multiple is always even will appear from considerations given below.

As a characteristic of this form of forced oscillation, it will be sufficient to remark that previous to the stage of steady main-

tenance, the vibration is intermittent with beats whose frequencies equal the difference of the frequencies of the system and the force.

As the frequency of the fork interrupter and hence of the periodic field is fairly high in comparison with that of the pendulum, we might consider the impulses received by the end of the pendulum rod as sudden enough to be represented to have taken place while the pendulum is in isolated positions on its arc of swing $XBAY$ (fig. 2) separated by finite intervals, equal to the period of interruptions, such as $A, A_1, A_2, \dots, A_{n-2}, A_{n-1}, A_n; B, B_1, B_2, \dots, B_{n-2}, B_{n-1}, B_n$. XEY represents the limited region within which the attraction of the Electromagnet is perceptible,—usually small in comparison with the big amplitude of maintenance obtained in practice

The conditions requisite for maintenance, in view of the fact that a balance of impulse must be carried forward by the pendulum on both ways of its motion, through the zone of electromagnetic attraction, may thus be found out. It might reasonably be assumed that the attractions by the electromagnet of the pendulum rod are symmetrical¹ about EO , and fall off gradually in intensity till they vanish at X and Y . Further if for the positions A and A_1 , B and B_1 , $OA_1 > OA$ and $OB_1 > OB$, the cumulative effect of impulsive attractions of gradually increasing intensity received in positions B_{n-1}, B_n and A outweighs the counter attractions received in positions A_1, A_2, A_3 , and a balance of impulse is carried forward. Similarly for motion of the pendulum towards Y , an identical state of things happen if $BO = OA$. In actual practice, the number of positions included within the zone of electromagnetic attractions are few (not more than four in all) and so the case is much simpler than that discussed here.

The number of A_1, A_2, \dots, A_n and B_1, B_2, \dots, B_n positions are evidently equal from symmetry and is each an integer (1, 2, 3, etc.) depending on the actual angular amplitude at which maintenance is obtained. Thus taking the two positions A and B

¹ That the impulses received by the maintained pendulum are of the nature contemplated, may be gathered by suspending the pendulum from the side of a projecting wooden beam, when the rhythmic character of the reactions on the support due to symmetrical impulses, would be plainly heard on putting the ear close to the projecting end of the beam, to afford a striking contrast to the irregular jerking at stages when maintenance is not obtained.

into consideration, the total number of such positions in a period of the pendulum is $2n+2$; which is always even. Thus maintenance is obtained only for even submultiple ratios of the periods of the field and of the pendulum and hence of their frequencies

Frequency ratio and amplitude

From the conditions already obtained for maintenance, it follows that the frequency of the interruptions being kept constant, maintenance might be obtained of the same pendulum at various amplitudes so as to alter the frequency ratio by successive additions or subtractions in its denominator of the number 2, as we can make additions or delete equal portions of the arc $XBAY$ (fig. 2) from its ends so as to include or exclude every time a single position of the pendulum on each side, without interfering with the maintenance. These deductions of theory fully explain the facts of observation already noticed that maintenance might be obtained of the same pendulum for two or more amplitudes, the actual drawback in obtaining the theoretically great number of such maintenances lies in the fact that the phase of passage of the pendulum in relation to the periodic magnetic field differs for different angular amplitudes of maintenance, thus necessitating a readjustment of the positions of affairs within the zone of the electro-magnet, and making actual adjustment for maintenance a matter of chance.

Free period of the pendulum and amplitude

The experimental results obtained as to the variation of amplitude of maintenance for the same frequency ratio admits of a simple explanation in the light of the theory indicated above. The general results obtained both by the author and Mr. Dey, shew the increase of amplitude for decrease in the free period (*Vide* Table II). The period of the interrupter remaining the same, it would follow from fig. 2, that if the period of the pendulum be increased the actual distances between consecutive positions A_1 , A_2 , A_3 , etc., must decrease, to keep the number of such positions to a defined integral value for the same frequency ratio; thus decreasing the amplitude for maintenance.

Phase-difference between the field and the pendulum

In the diagrammatic scheme (fig. 2) we have assumed that O , the position of equilibrium of the pendulum lies asymmetrically

with regards to positions A and A_1 or B and B_1 , or in other words the pendulum passes its equilibrium position, assymmetrically with regard to two successive positions of maximum magnetism. Photographic studies of phase confirm these hypotheses, as assymetry is considerable for comparatively large amplitudes of maintenance. As regards small amplitudes of maintenance the assymetry is less marked and the pendulum passes its equilibrium position at about the midway between two maxima. These facts explain to a great measure, the slight attractive forces of the electromagnet for smaller amplitudes and greater attractive for bigger amplitudes, thus making the decrease in the free period nearly the same for bigger than as for smaller amplitudes as in fig. 1

V.—DISCUSSION OF THE MATHEMATICAL THEORY.

It has tacitly been assumed in developing the theory already given that the energy lost by dissipation is just compensated by the flow of energy from the field. The dynamical theory given by Prof. C. V. Raman admits of quantitative evaluation of the flow and the loss by dissipation. The system having one degree of freedom its equation of motion is written in the form

$$\ddot{\theta} + k\dot{\theta} + [n^2 - \sigma\theta^2 + f(t)F(\theta)]\theta = 0 \quad \dots \quad (1)$$

Now assuming the maintained oscillation of the pendulum to be represented by

$$\theta = \psi_1 \sin (\rho t + \epsilon_1) \quad \dots \quad (2)$$

it can be easily shown that the rate of loss of energy due to dissipative forces

$$= \frac{1}{2} k \rho^2 \psi_1^2 \quad \dots \quad (3)$$

and the energy which flows from the field to the pendulum, on the assumed mode of vibration in which $m=2s\rho$, where S is an integer,

$$= \frac{1}{2} \rho \psi_1^2 \gamma F(\theta) \left[\frac{\sin (2\rho + m)T \cos \frac{m}{\rho} \epsilon_1}{2\rho + m} - \frac{\cos (2\rho - m)T \sin \frac{m}{\rho} \epsilon_1}{2\rho - m} \right]$$

where

$$= \frac{1}{\rho} \sin^{-1} \frac{\rho}{\psi_1} \dots \dots \dots (4)$$

ϕ being the angular distance within which the force of the electro-magnet is perceptible. The constants in the expressions (3) and (4) may be determined in the following way

K.—The logarithmic decrement of oscillations of the pendulum is determined, while it is being damped by the interrupted field of the magnet about the amplitude at which maintenance is obtained. K is known from the relation $\log\text{-decrement} = \frac{1}{4} KT$, where T is the period of the pendulum for the amplitude of maintenance. (The logarithmic decrement instead of being found by the tedious process of recording successive amplitudes, is determined quickly without seriously affecting the accuracy from the time (t) in which an amplitude falls to $\frac{1}{e}$ th its value, the log-decrement being then equal to $\frac{2T}{t}$)

ϕ and ψ_1 are given by $\frac{2\pi}{\text{period}}$ and the circular measure of the amplitude respectively

$\gamma F(\theta)$ —to one end of a spring (a hack-saw blade) a few cms. of the pendulum rod is fixed by soldering (the frequency of the combination being about 60 per sec.) This is clamped in a vice and hangs over the electromagnet, with the rod in position of the pendulum. The interrupter being worked the amplitude of oscillation of the spring is measured on the scale of a microscope focussed onto a fine luminous point on the rod. The deflecting force corresponding to the amplitude is measured by deflecting it statically by known weights placed on a scale pan attached to the pendulum rod by a string passing over a pulley. The actual value of the deflecting force or in other words, the amplitude of the oscillating spring varies slightly with different angular positions of the spring with respect to that of the electromagnet, and the mean value of several such deflecting forces is taken as the measure for $\gamma F(\theta)$

ϵ_1 —Determinations are made as described in Section 3, page 149

ρ and $m - \frac{\rho}{m}$ being equal to the 'frequency ratio' of maintenance is known by determinations of the period of the pendulum that of the interrupter being known from previous determinations.

T is calculated from the relation $T = \frac{1}{p} \sin^{-1} \frac{\phi}{\phi_1}$ where ϕ is determined approximately by deflecting the pendulum by weights attached to the end of a string passing over a pulley, while (i) the interrupter is working, (ii) the interrupter is not working. The meeting point of the two curves to represent the deflecting weight against deflection, on the same scale gives the value of ϕ . Thus it has been calculated that for the case $m=36 p$.

Amplitude of maintenance	Energy lost by dissipation in ergs per sec	Energy gained from field in ergs per sec
39°	0.231	0.264
22°	0.071	0.082
12°	0.016	0.020

VI.—SUMMARY AND CONCLUSION.

1. The maintained oscillations of a subsynchronous pendulum which was noticed and investigated by Lord Rayleigh and later by Mr. Dey and Prof. C. V. Raman, have been studied with a 35 cms. iron-rod pendulum and an interrupter fork of frequency 32

2. The exact equality of the ratio of the frequency of maintenance of the pendulum to that of the interrupter fork to one or other of the 'frequency ratios' for slight variations in the temperature of the room, is established by measurement of the absolute frequency of the fork by chronographic records.

3. Some of the characteristics of subsynchronous maintenance are—

(a) maintenance of subsynchronous pendulum may be obtained at two or three different amplitudes, when the position of the bob on the pendulum and the frequency of the interrupter are not interfered with.

(b) maintenance is not possible for very large and for very small amplitudes.

(c) the free and the forced period of the subsynchronous pendulum for different amplitudes, obtained by altering the frequency of the interrupter differs but slightly from each other, the difference being the same for big as for comparatively small amplitudes.

(d) Results obtained by altering the position of the bob on the other hand, shew increase of amplitude of maintenance for decrease in the free period.

(e) A method has been developed for determining by photographic record, the phase of passage of the pendulum through its equilibrium position in relation to the periodic magnetic field. The phase-angle is almost zero for small amplitudes and attains the value $\frac{\pi}{2}$ for very big amplitudes.

4. From a simple theory of subsynchronous maintenance on the basis of the impulsive nature of the attraction of the electromagnet on the pendulum and the limited zone of action of the electromagnet through which energy required to counteract dissipation is supplied, the condition requisite for maintenance is found to be that the two consecutive attractions near the equilibrium position of the pendulum are asymmetric about the mean-position. The theory explains primarily the even submultiple ratio of frequencies necessary for maintenance. It explains the facts of observation in 3(a) and 3(d). The assumed asymmetry of theory is brought out by the photographic records of phase and the nature of asymmetry observed explains the result noticed under 3(a).

5. The expressions of the mathematical theory for the dissipation and the flow of energy from field, have been evaluated for a few cases and there is a fair agreement between the two values.

The work was carried on in the Laboratory of the University College of Science and the writer, in conclusion, wishes to express his best thanks to Prof. C. V. Raman for suggestions and guidance.

XV. On Whispering Galleries.

**By C. V. Raman, M.A., Hon D.Sc., Palit Professor of
Physics in the Calcutta University.**

(Plates X, XI, XII, XIII and XIV.)

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I —INTRODUCTION

In the volume of collected papers on Acoustics by the late Prof. W. C Sabine published recently by the Harvard University, there is a very interesting article on 'Whispering Galleries' in which the architectural and acoustical features of several remarkable structures in Europe and America have been discussed. No mention is however made of whispering galleries in other parts of the world. Among the Indian whispering galleries the most notable, architecturally and acoustically, is the great Gol Gumbaz at Bijapur. In the Victoria Memorial recently completed at Calcutta, there are two very fine whispering galleries, one of which, curiously enough, remained unsuspected till it was discovered by the writer. There is also another whispering gallery at the Calcutta G P.O., also first noticed and studied by the writer. The acoustical properties of the building known as the Government Granary at Bankipore in Patna District are also of much interest. The present paper contains a description of these whispering galleries. Other acoustical curiosities, such as Sekundar's tomb at Fatehpur Sikri near Agra, have been brought to the writer's notice, but they are not here discussed.

While in England in the year 1921, the writer in collaboration with Mr. G. A. Sutherland of the University College, London, had an opportunity of carrying out a study of the well-known whispering gallery in the Dome of St. Paul's Cathedral at London, and the results of the investigation showed the presence, with a steady source of sound, of an interference-field in the gallery with radial and circumferential nodal lines.¹ The comparative study of the three whispering galleries at Calcutta conveniently accessible to the writer has brought to light some further facts of interest relating to these structures. These are also discussed in the paper.

II —THE GOL GUMBAZ AT BIJAPUR (See Plate X)

"Transcending all other buildings at Bijapur in simple mass, and dominating the landscape for miles around, the great Gol Gumbaz or tomb of Sultan Muhammad,² stands alone (Plate X). For size, few other buildings in India can be compared with it. Its noble proportions and magnificent dome are only seen to the fullest advantage from a distance. When close up to it, the dome seems to sink into the building, and to require an intermediate terrace or storey to raise it into full view. A few extra feet here would certainly have improved the general design, even when viewed from further off. The impressive grandeur of the building and its imponderable mass simply overwhelm the spectator with awe. It stands in the extreme east end of the city, its massive basement resting upon the solid rock. The vast mausoleum stands out with most striking effect when viewed, as Muhammad himself must often have seen it, from the upper hall of the Athar Mahall, when, backed by great storm clouds, the low western sun suddenly bursts through a rent and illumines the great building. It then flashes out into brilliant contrast against the rolling masses of angry black clouds; the mellow tints of its walls are bathed in a golden glow, and the great dome shines like burnished brass. Under all this glory peacefully repose the remains of Sultan Muhammad.

"King Ibrahim, his father, had raised the beautiful pile of the Ibrahim Rauza, which was the last word in decorative and luxurious magnificence. It was impossible for Muhammad to go further

¹ *Nature*, Sept. 1921, and *Proc. Roy. Soc.* 1921.

² *King of Bijapur in Southern India, seventh of the Adil Shahi Dynasty, from 1627 to 1656.*

upon the same lines, so he struck out in a different direction altogether, and endeavoured to dwarf it, and everything else, by stupendous mass; and this he certainly accomplished. The Gol Gumbaz is the antithesis of the Ibrahim Rauza in that the strong virility of conception of the one contrasts with the delicate femininity of the other. His reign of thirty years, however, was not sufficient wherein to fully complete the building, for he seems to have died while the plastering of the walls was in progress, and it was no one else's business to complete what he left unfinished. One cannot help wondering what new departures would have

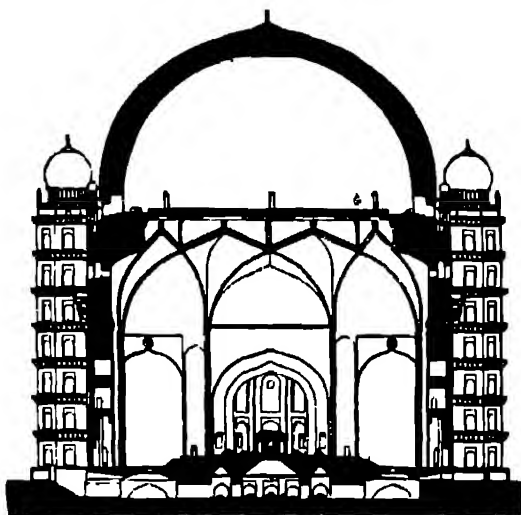


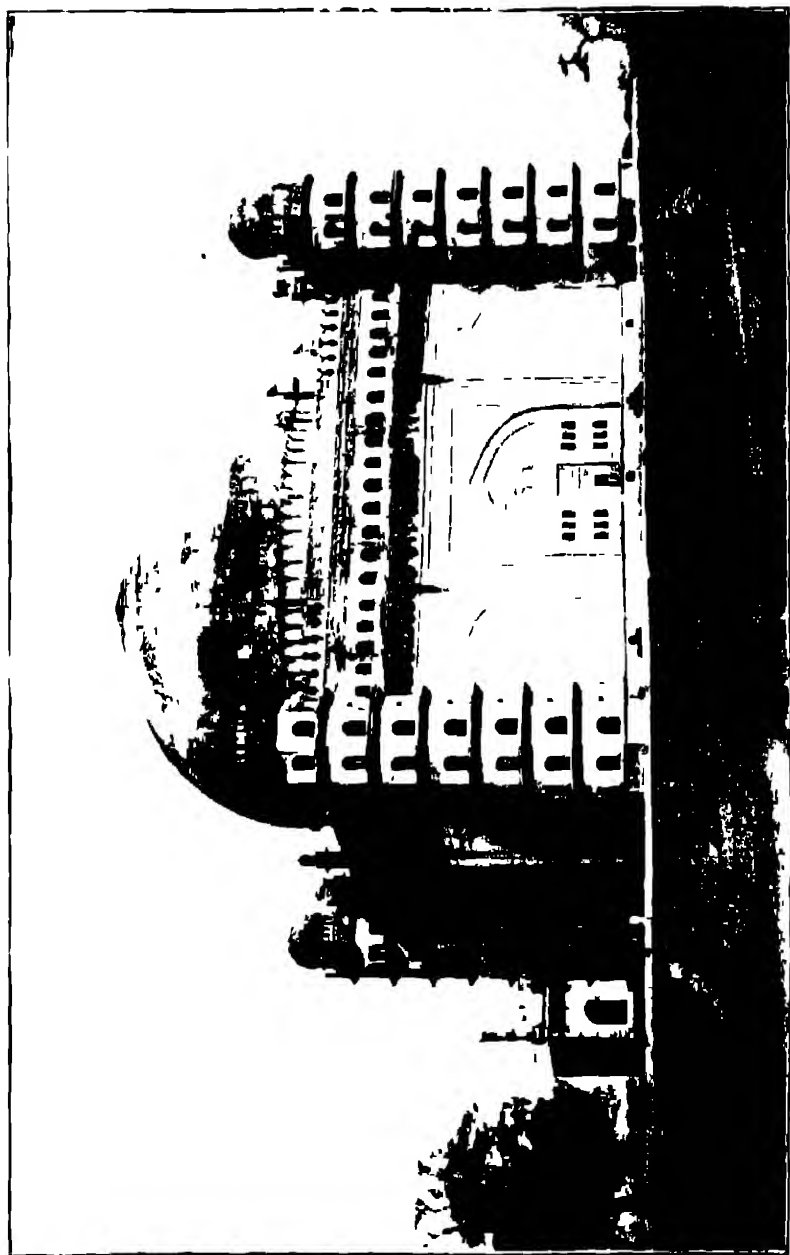
FIG. 1. The Gol Gumbaz at Bijapur (Architectural Drawing)

been made in the further development of Bijapur architecture had the dynasty lived and flourished another hundred and fifty years, for they were daring builders.

"A glance at the plan (Fig. 1) of the Gol Gumbaz shows what a simple building it is for all its size—just a great square hall, enclosed by four lofty walls, buttressed up by octagonal towers at the corners, and the whole surmounted by a hemispherical dome. The great size of the dome, and the neat and perfect manner in which, by means of cross arching and pendentives, the square walls have been worked up to meet it, are the most notable features of the building. The extreme outside measurement of the mauso-

leum including the towers is 205 feet square. The extreme height to the apex of the dome from the base of the building is 198 feet 6 inches; the exterior diameter of the dome is 144 feet while the interior diameter, measured 124 feet 5 inches, and the great hall, below, with no intermediate supports of any kind, inside its walls, is 135 feet 5 inches square. The interior height, from the level of the floor, around the tomb platform to the top of the dome is 178 feet. Within the base of the dome is a broad gallery, 11 feet wide, which hangs out into the interior of the building, 109 feet 6 inches above the floor. Narrow staircases wind up through the corners of the building where the towers join it, and passages lead out from them on to each of the pigeon-holed storeys of the towers. In the centre of the floor of the hall is a high platform upon which are the counterfeit domes, the real graves being in the vault underneath which extends over the whole length and breadth of the hall.

"Each of the four walls of the building had been raised as three great arches, the central one being wider than the two side ones, and these have been filled in with rubble masonry in the side ones, and cut-stone in the central one. On the north side, however, the central archway had been left open, or had been subsequently opened, as a small chapel or chamber has been built against the wall here as an annexe, communicating through the arch with the great hall within. In the central archways of the other three sides are the doors and windows; but, even here, the filling in above the windows can only be called crazy or patchwork-masonry. The masonry of the great dome may be looked upon as practically concrete it being composed of bricks in mortar, the thickness of the shell varying from ten feet at the springing to nine feet near the crown. It is thus a great rigid concrete shell without voussoirs, and, consequently, with practically no side thrusts of any kind so long as it remains intact. It is a dead weight acting vertically downwards partly upon the cross arching within and partly upon the side walls just as an inverted china basin would act upon the upper edges of a cube upon which it might rest. Being built in this way, with ring upon ring of thick brick work, each corbelled forward until they close at the apex, it is probable that no centering or support was needed beneath it during construction, except, perhaps, for a small section near the crown, which would have been supported by that part of the dome



The Gol Gumbaz at Bijapur

already built. An outward thrust that could possibly come upon the side walls would be amply neutralised by the weight of the material in the pendentives which hang over inside the building.

"This system of pendentives is, without doubt, the most successful and most graceful method of construction for such domes. It obviates any interference with the external contour of the dome, and adds, at the same time, a very pleasing feature to the interior—the interlacing or groining of the arches. The tendency of the dome to spread at the base, which is counteracted by the pendentives and great mass of masonry thus thrown into the interior of the building, was guarded against, in case of the Pantheon at Rome, which possesses a dome of greater diameter, by the heaping up of masonry upon the haunches of the dome outside, thus destroying its beauty of outline.

'The great hall below, which is covered by the dome, covers an area of 18,337·67 square feet, from which if we take 228·32 square feet for the projecting angles of the piers carrying the cross arches, which stand out from the walls into the floor, two on each face, we get a total covered area, uninterrupted by supports of any kind, of 18,109·35 square feet. This is the largest space covered by a single dome in the world, the next largest being that of the Pantheon at Rome, of 15,833 square feet. If we add the pendentives to the actual dome, to which they naturally belong as part of the superstructure, this then becomes the greatest domical roof in the world.

"But, was not this great dome, after all, but an after-thought?... Before the walls of the Gol Gumbaz had risen many feet, it would seem that the plans were altered. The daring spirit of the architect, urged on perhaps by Sultan Muhammad himself, incited him to attempt the more stupendous task of hanging a mighty dome right across the whole expanse of the outer walls; and it seems almost incredible that the man who conceived, and carried to such a successful issue, this magnificent project, should have passed into oblivion; his very name is unknown.

"Another remarkable feature in the building is its whispering gallery, which runs round, inside the dome, at its base. Access is gained to it from the terraced roof around the base of the dome, by eight small door ways through it. As may be seen from the section (Fig. 1) it hangs out into the building, being

supported upon the crowns of the cross arches below ; and it is about eleven feet wide, inside the low parapet wall which protects it. On entering the building a person is struck by the loud echoes which fill the place in answer to his footfall ; but these sounds are intensified on entering the gallery. The footfall of a single individual is enough to wake the sounds as of a company of persons, and, in response to ordinary conversation, strange weird sounds and mocking whispers emanate from the wall around. Loud laughter is answered by a score of friends safely ensconced behind the plaster. The slightest whisper is heard from side to side, and a conversation may be easily carried on across the diameter of the dome, in the lowest undertone, by simply talking to the wall, out of which the answering voice appears to come. A single loud clap is distinctly echoed ten times "

The foregoing description extracted from the volume on Bijapur architecture by Mr. Cousens published in the Indian Archaeological Survey series makes it clear that the whispering gallery at the Gol Gumbaz is a very remarkable one. The present writer has not yet had an opportunity of visiting it but hopes it will soon arise. It is clear that the architectural features of this whispering gallery are distinctive, situated as it is at the foot of the dome itself, instead of in a drum below it as at St Paul's, and a fuller study of the acoustical results following from this feature would be well worth while. Judging from the case of the whispering gallery at the Victoria Memorial, Calcutta, to which reference will be found below, it is not improbable that in addition to the usual circumferential propagation of sound-waves round the gallery, there will also be found a local concentration of sound at the further end of the diameter at which the source is situated. Mr. Cousen's description indeed suggests that such an effect is present in a notable degree.

III — THE VICTORIA MEMORIAL AT CALCUTTA. (Plate XI.)

The Hindu and Moslem Rulers of India left behind them great architectural monuments which impress the imagination of the beholder, and, in not a few cases, are gems of perfection which command the admiration of the world, e.g., the Taj Mahal. Though not on the same level as these triumphs of indigenous art in greatness of conception or execution, the Victoria Memorial

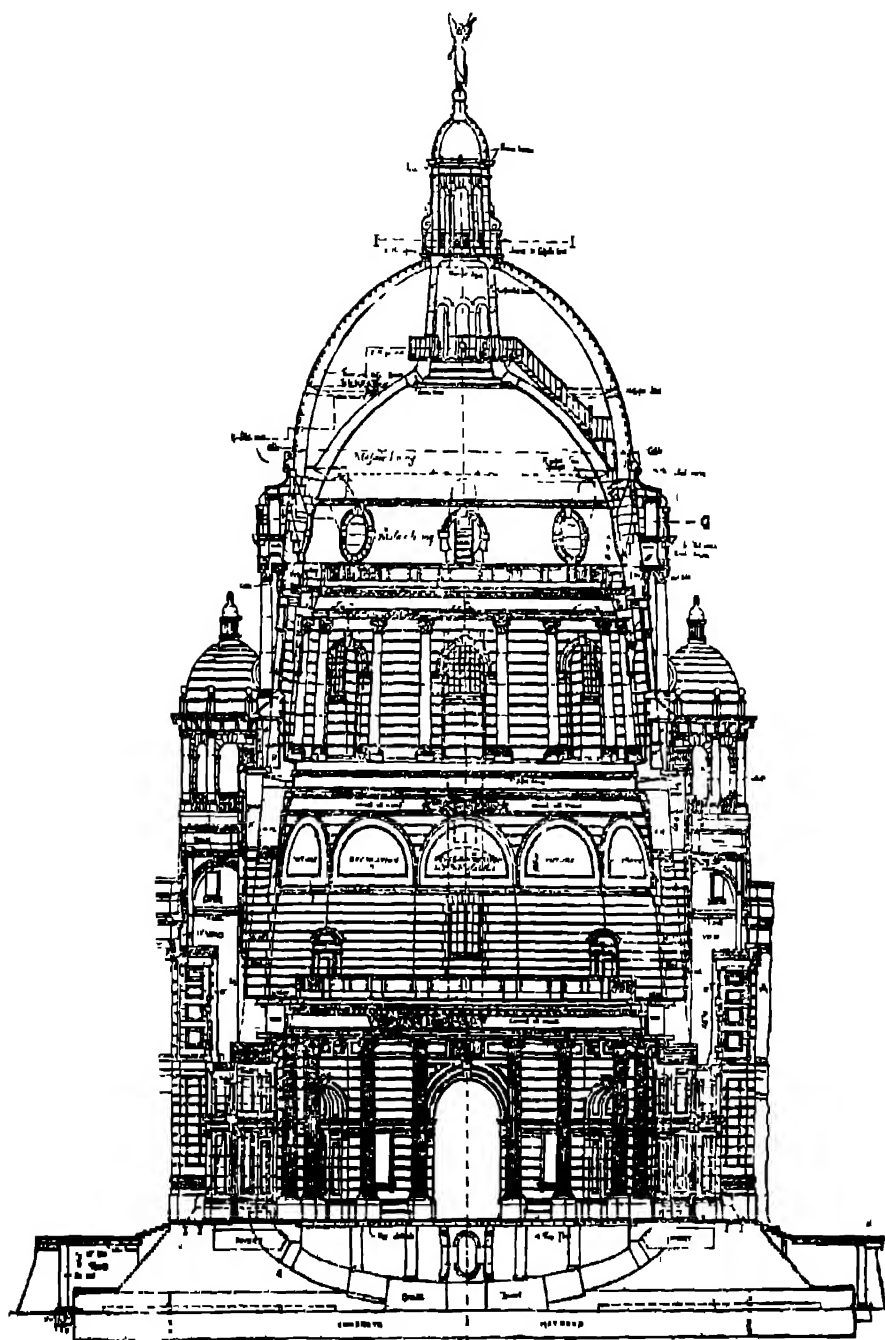
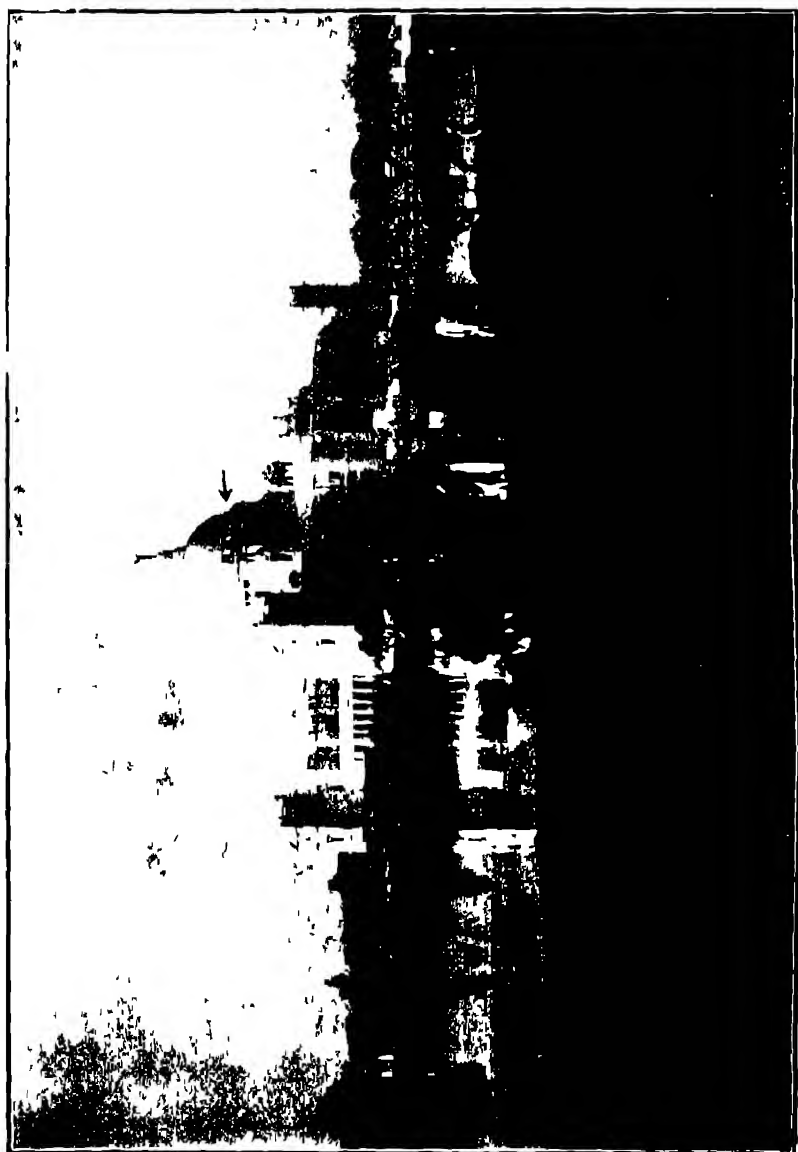


FIG. 2. Section of the Victoria Memorial showing double dome.

recently completed at Calcutta, may, nevertheless, claim to be the most remarkable building of any erected in India during the years of British Rule and it is certainly an ornament to the "City of Palaces" Occupying a privileged position in the Maidan or open space between Fort William and the city, this edifice of white Indian marble with its dome and winged statue of victory crowning all, catches the eye from afar and is a worthy monument of the reign of the Queen whose memory it seeks to perpetuate The building took twelve years to construct and cost over half a million sterling It is intended to be a treasure-house for historical paintings, sculptures, and other relics, and stands in extensive grounds which are being laid out as a public garden with ornamental tanks and bridges

Going up by the grand stair-case facing the Maidan towards the Ochterlony monument, and passing through the portico and entrance room, the visitor finds himself in the circular Queen's hall which stretches up from the floor to the base of the inner dome of the building In the centre of this stands the statue of the young Queen Victoria Some 35 feet up from the floor is a gallery with its walls forming a dodecagon and above this, on the wall, twelve semi-circular spaces covered with paintings representing her life Still higher, some 95 feet from the floor, is a second circular-gallery four feet broad which lies just at the base of the inner dome and is surrounded by a marble railing. The circular wall of the gallery here has a very decided slope inwards and is interrupted some few feet above the floor of the gallery by seven great circular windows which are visible from outside and by the opening for the stair-case by which admission to this gallery is obtained. An opening is also provided above by which it is easy to enter the space between the two domes and pass round it by a circular foot-path. The inner dome is open at the top to which access can be obtained by stairs. These features are indicated in the architectural section in Fig. 2.

The circular gallery at the base of the inner dome, and the space between the two domes form two very perfect whispering galleries, the former of which was first discovered by the writer. The diameter of the former is 59 feet and of the latter 56 feet. Their special acoustical features have been studied by the writer and will be referred to more fully in Section V below.



The Victoria Memorial at Calcutta

IV.—THE GRANARY AT BANKIPORE (PATNA) (See Plate XII)

"At once the most prominent and the most curious building in Bankipore is the old Government Granary known as the Gola. This is a brick building, 96 feet high with walls 12 feet thick at the bottom, built in the shape of a beehive or half an egg placed on end, with spiral two stair-cases on the outside winding to the top; it is said that Jang Bahadur of Nepal rode on horse-back up one and down the other. This dome shaped structure was erected sixteen years after the great Famine of 1770, as a store-house for grain, it being intended that the grain should be poured in at the top and taken out at the bottom through the small door there. Owing to a curious mistake on the part of the builders, these doors were made to open inwards. The following inscription is on the outside —

"No. 1 In part of a general plan ordered by the Governor-General and Council, 20th of January, 1784, for the perpetual prevention of Famine in these provinces, this Granary was erected by Captain John Garstin, Engineer. Completed the 20th of July, 1786. First filled and publicly closed by——"

The store-house has never been filled and so the blank in the inscription still remains, while the opening at the top is closed by a great stone slab. It stands to this day the monument of a mistake. During the famine of 1874, a quantity of grain, which, if left at the railway station might have been injured by the rain was temporarily stored there, and in times of scarcity proposals are still made to fill it with grain. But the loss from damp, rats and insects renders such a scheme of storing grain wasteful and impracticable. This building, once intended to meet the requirements of the whole district in time of famine, is now only useful as a store-house for furniture. It is chiefly remarkable for its reverberating echo, which answers to the slightest sound, a whisper at one end being repeated at the other. It is a landmark for a considerable distance along the river and commands a fine view of the surrounding country."

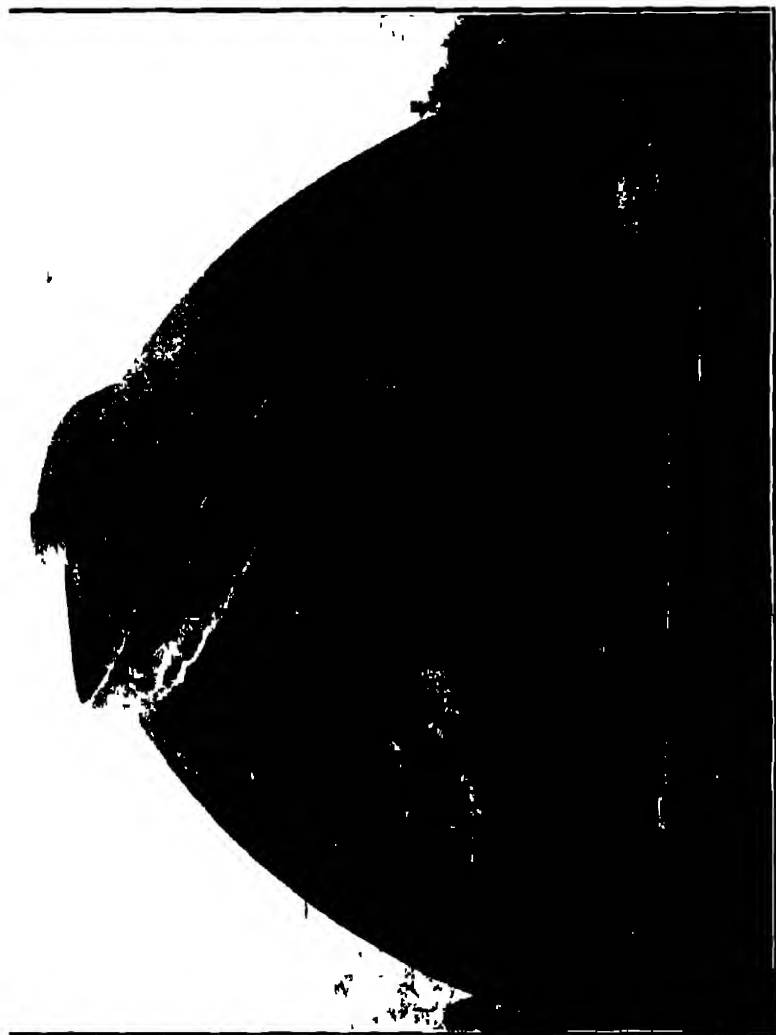
The foregoing description is taken from the Patna District Gazetteer. In September 1922, the writer paid a brief visit to Bankipore and looked over this building, but had no time to make a thorough scientific examination of its acoustics. This is obviously

a task that ought to appeal to the physicists at the local University of Patna. The most striking acoustical feature that was noticed by the writer was the return of the sound from the walls of the building as a surprisingly loud single echo when the observer stood at its centre and uttered a syllable or two. This was evidently due to the curved walls acting as a concave mirror focussing the sound at the same point as its origin. When the observer moved away from the central position, the simple return of sound gave place to a multiple echo.

The interior of the building is rather gloomy, as it is lighted only through the four doors in its massive brick walls. Inside, the brick work is bare, and has not been plastered over. The surface of the wall is thus not particularly smooth. An attempt to carry on a conversation in a low undertone with another observer situated 90° off along the curved wall was only partially successful. A further thorough study of the acoustics of this structure would be well worth while in order to explain the formation of the curious echoes heard in it.

V —WHISPERING GALLERY AT THE CALCUTTA GENERAL POST OFFICE (See Plate XIII.)

This gallery whose acoustical properties were first discovered by the writer merits a brief description. The General Post Office is the most imposing building amongst the many stately piles that surround Dalhousie Square at Calcutta. It is crowned by a dome set on a high cylindrical drum, the upper part of which is occupied by a row of windows which illuminate the building, the lower part of the drum consists of a perfectly vertical smooth circular wall some fifteen feet high. This is provided with a gallery four feet broad to which admission is obtained through a single door, which opens in from the terrace of the building. The diameter of the gallery is 57 feet. Immediately below the gallery is the public rotunda. Unfortunately owing to the location of the building and one side of the rotunda being open towards Dalhousie Square, the drum of the dome is full of the hum of public traffic throughout the day. But early in the morning or late in the evening when the bustle of traffic has died away, the whispering gallery is fully worth a visit by the interested student of physics. It shows effects similar to those observed at St. Paul's though not in such a high degree.



The Granary at Bankipore

VI.—PROPAGATION OF SOUND IN WHISPERING GALLERIES.

The comparative study of the three whispering-galleries at Calcutta has yielded result of interest. The three galleries are approximately of the same size; the differences in their architectural characters are however considerable, and the differences in their acoustical characters consequent thereon are quite distinct. The gallery at the Calcutta General Post Office is architecturally very similar to that at St Paul's in London, though smaller in size, with the important difference that its walls are perfectly vertical while those of the St. Paul's gallery slope distinctly inwards as has been pointed out by Prof Sabine in his article. The fact that the effects observed in the latter are clearly more striking appears to support Prof Sabine's contention that the inward slope of the wall is an important feature contributing to the efficiency of the whispering gallery.

The lower gallery at the Victoria Memorial whose acoustical features were first observed and studied by the writer has quite distinctive features of its own. This gallery is just below the inner shallow dome, and its wall is broken by eight large openings. In fact the continuous part of the wall above the floor of the gallery is only three feet high. Nevertheless, the gentlest whisper at any part of the wall is heard right round the gallery, particularly if the observer and his assistant stoop down a little towards the floor. The effect is hardly less striking than that observed at St. Paul's. As the wall of the gallery has a very marked slope inwards, this appears to furnish further support for Prof. Sabine's views. Part of the effect is however doubtless due to the presence of the curved surface of the dome above, of which indeed the wall of the gallery practically forms a part. If the observer and his assistant both stand up to their full height, and face each other directly, it is distinctly easier to converse in an undertone when they are at the opposite ends of a diameter than when they are a smaller distance apart.

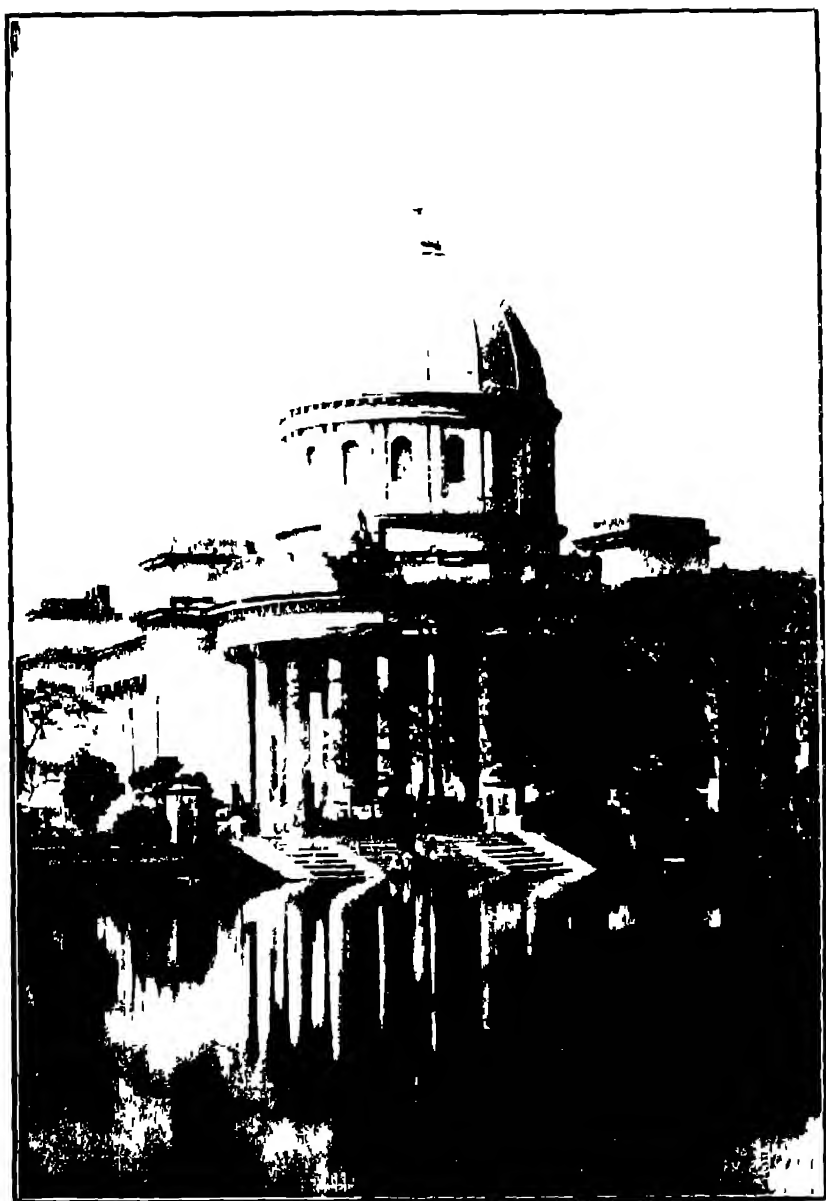
The upper gallery at the Victoria Memorial which lies between the two domes naturally shows very striking effects, owing to the comparatively enclosed character of the space; the ease with a whisper any where is heard throughout is distinctly uncanny, particularly as the observer and his assistant are hidden from each other by the mass of the inner dome. As will be seen from the

architectural section, the wall of the gallery slopes pretty steeply inwards even at the lowest point.

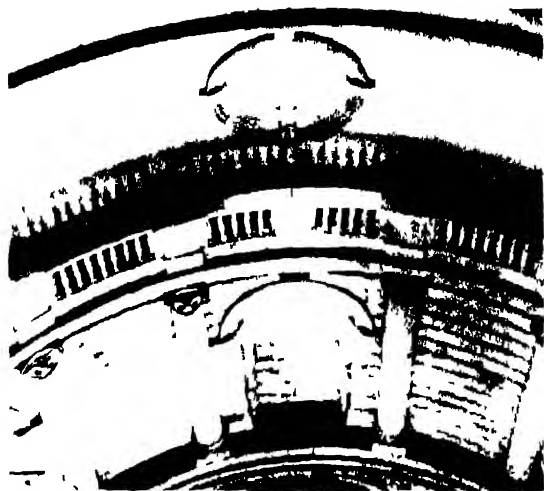
Experimenting in these whispering galleries, the existence of circumferential and radial nodal lines in the acoustical field due to a steady source of sound was established as in the case of the St Paul's gallery. Another interesting point to which the writer has not seen attention previously directed is the study of the propagation of sounds of an *impulsive* character in whispering galleries. Visitors to St Paul's notice immediately the peculiar multiple echoes which accompany the sound of footfalls in the gallery, a single hand-clap is repeated five or six times. The echoes appear to proceed from somewhere near the opposite point of the wall of the gallery. Similar multiple echoes are noticed in the Calcutta galleries, the effect is least marked in the General Post Office gallery, much better in the lower gallery at the Victoria Memorial and appears in an extraordinarily exaggerated form in the upper gallery between the two domes, a single hand-clap or other sharp sound produced in the gallery being heard repeated no fewer than twenty times. As the observer producing the sound mounts the stair towards the top of the inner dome, the effect becomes less and less striking and ultimately vanishes at the centre. These observations give the clue to the real nature of the phenomenon, the multiple sound is not due to any echo, but is merely due to the fact that a sound-wave generated at any point on the gallery travels circumferentially round and round the gallery many times and is heard each time it passes the observer before it finally ceases to be audible. The smaller the decrement of intensity between two successive returns, the greater is the efficiency of the whispering gallery. The character of the sound at each successive return also undergoes a distinct alteration, as of course is to be expected owing to the differing decrements for sounds of different pitch.

The foregoing simple explanation of the multiple sounds

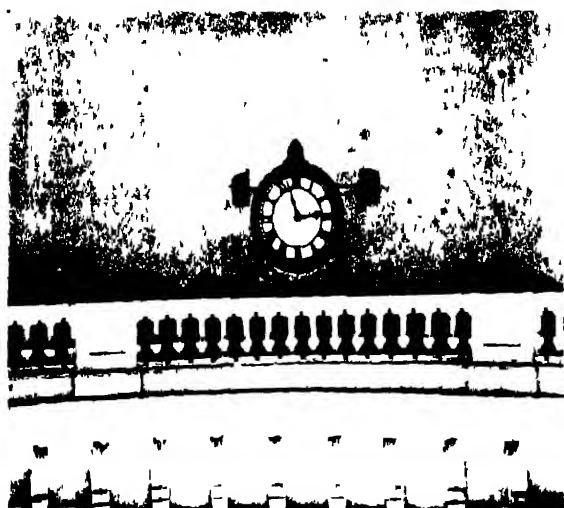
ent points in the gallery, the sound waves moving in opposite directions would pass the observer at different instants, and the rate of multiple sound is slowest when the observer is at the centre and the source is exactly at opposite ends of a diameter. This



The Calcutta General Post Office.



Part of circular gallery at the Victoria Memorial



Part of circular gallery at the Ceylon General Post Office

was actually found to be the case, and the relative intensities of the sounds and the points of the gallery from which they appeared to emerge showed curious variations as the position of the observer was shifted

The second method of verification was to determine the time interval between successive returns of the sound. With a little practice, this could be done in all the three galleries and was a particularly easy task in the upper gallery of the Victoria Memorial. By giving a tap periodically say at each tenth return of the sound, the succession could be kept up indefinitely, and the time taken for a few hundred returns of the sound could be determined with a stop-watch. The interval between successive returns of the sound was found to be equal to the circumference of the gallery divided by the velocity of sound, correct to within one per cent. It would be interesting to repeat this experiment in the larger galleries at St. Paul's and the Gol Gumbaz at Bijapur

VII.—SYNOPSIS

The paper describes five whispering galleries. (1) the Gol Gumbaz at Bijapur, (2) the upper gallery between the two domes of the Victoria Memorial at Calcutta, (3) the lower gallery under the inner dome of the Victoria Memorial; (4) the Granary at Bankipore, and (5) the gallery at the Calcutta General Post Office. Of these (3) and (5) were discovered by the writer, and in quality, (3) is not greatly inferior to the gallery at St. Paul's at London.

The comparative study of (2), (3) and (5) has led to some interesting results, notably the confirmation of Sabine's view of the importance of an inward slope of the wall of the gallery for giving the best effects, and the concentration by a spherical dome of a maximum of sound at the opposite end of the diameter. Circumferential and radial nodal lines were observed in these galleries similar to those observed at St. Paul's. Further, the study of the propagation of impulsive sounds in these whispering galleries showed that the multiple sounds heard are not echoes as might be thought at first, but are due to the fact that the sound-wave travels circumferentially round the gallery several times before it is sensibly extinguished, and is heard each time as it passes the observer. The smallness of the decrement in successive returns is a measure of the strength of the whispering gallery effect. The

interval between successive returns is equal to the circumference of the gallery divided by the velocity of sound within an accuracy of one per cent. The waves travelling in opposite directions round the gallery can be differentiated by ear.

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CORRECTION SLIP

Page 17, last line

for
$$\frac{\pi^2}{2n_0\lambda^4} (K_0-1)^2 \quad \rightarrow \quad \frac{(9-4\gamma)}{6-7\epsilon_1}$$

read
$$\frac{\pi^2}{2n_0\lambda^4} (K_0-1)^2 \quad \rightarrow \quad \frac{(9+4\gamma)}{6-7\epsilon_1}$$

Page 22, on line 8

instead of

$$\frac{\pi^2}{2} \frac{(K_0-1)^2}{n_0\lambda^4} \quad \frac{2_1}{6-7\epsilon_1}$$

read

$$\frac{\pi^2}{2} \frac{(K_0-1)^2}{n_0\lambda^4} \quad \frac{2_1}{6-7\epsilon_1} (4\gamma-3)(1+\cos^2\phi)$$

Page 70, third line from bottom

instead of $\epsilon/2$

read $\epsilon_1/2$

1. Electromagnetic Theory of the Scattering of Light in Fluids.

By K. R. Ramanathan, M A.,
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Received for publication, 11th November, 1922

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- 1 Introduction
- 2 Continuous Medium Theory
- 3 Scattering by Isotropic Molecules.
4. Scattering by Anisotropic Molecules
- 5 Comparison with Experiment
- 6 Synopsis

1 INTRODUCTION

The subject of "Molecular Scattering of Light" whose foundations were laid by the late Lord Rayleigh, gained a new significance from the experimental work of Cabannes¹ and the present Lord Rayleigh² on the scattering of light in dust-free gases. Its importance was further increased by Prof Raman's³ application of Einstein's investigation of critical opalescence to the case of scattering in fluids in general, and his explanation of the blue of the sea as being caused by molecular scattering of light in water. Experimental work by the present author⁴ on the

¹ Cabannes—Ann. Physique, Tome XV, 1920, pp. 1-150

² Rayleigh—Proc. Roy. Soc. A, 1918, p. 151

³ C. V. Raman—Proc. Roy. Soc. A, April, 1922, p. 65 and, 'Molecular Diffraction of Light,' Calcutta University Press, 1922

⁴ K. R. Ramanathan—Proc. Roy. Soc. A, 1922, p. 151.

scattering of light in ether and by Mr R Venkateswaran¹ in normal pentane showed that throughout the range of temperatures from 35°C to the critical point, both in the saturated vapour state and in the liquid state in equilibrium with the vapour, the intensity of scattering in a transverse direction is given by the Einstein Smoluchowski expression (with a correction for admixture with unpolarised light)

$$I = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2$$

where I is the intensity of the scattered light from a unit volume at a large distance r from the volume.

R , N are the gas-constant and the number of molecules respectively per gram-molecule

T is the absolute temperature

β is the isothermal compressibility of the medium

μ is its refractive index, and

λ is the wave-length of the incident light

The above expression was derived by Einstein on the assumption that the scattering of light was caused by the local changes in dielectric displacement consequent upon the local fluctuations of density to which an otherwise uniform medium is subject owing to the thermal movements of its parts. In such a case, the light scattered in a direction transverse to the primary beam should be completely polarised. The same result may be deduced when the individual molecules are regarded as sources of scattered radiation provided that they are supposed to be spherically symmetrical and their restricted freedom of movement is taken into account. Actually, however, the transversely scattered light is in general found to be imperfectly polarised, much more so in a liquid than in its vapour. The imperfect polarisation has been explained

¹ R. Venkateswaran—Trans. Chem Soc., 1922, Vol 121, p 2655

by the late Lord Rayleigh,⁶ Born⁷ and Gans⁸ on the assumption of molecular anisotropy. The subject has also been studied by Sir J. J. Thomson⁹ from the point of view of the electron theory. The increase of imperfection of polarisation in the liquid state is remarkable and an explanation of it has been given by Raman on the idea that the scattering in a fluid can be considered to be made up of two parts, a density-scattering and an orientation-scattering of which the former is given by the Einstein-Smoluchowski formula while the latter is proportional to the density of molecules. It is obviously of importance to make an exact investigation of the connection between the state of aggregation of a medium and the quality of the scattered light, especially in view of the fact that it promises to throw light on the nature of the liquid state itself. In the following paper, an attempt is made to develop a general theory of scattering in fluids. In Article 2, the medium is assumed to be continuous as in Einstein's treatment of the subject, but subject to local fluctuations of density depending upon the laws of statistical mechanics. Lorentz's electromagnetic treatment of the scattering of light in gases developed in his book "*Les Theories Statistique en Thermodynamique*" has been adopted and extended to the general case of a fluid of any compressibility. In Article 3, the subject is treated from the molecular standpoint in the case when the molecules are isotropic and the Einstein-Smoluchowski formula for scattering is deduced. In Article 4, the molecular treatment is extended to the case when the molecules are anisotropic and expressions are deduced for the intensity of the scattered light, its state of polarisation and the co-efficient of extinction in the medium. In

⁶ Rayleigh—Phil Mag, XXX, 1918, and Scientific Papers, Vol VI, p. 340

⁷ Born—Verh. Deutsch. Phys. Gesell., Vol 10, p. 213, 1917, and Vol 20, p. 16, 1918

⁸ Gans—Ann. der Physik—10, 1931

⁹ Sir J. J. Thomson—Phil Mag, XL, 1920, p. 303

Article 5, the results are discussed with reference to experimental data as regards polarisation of the scattered light in liquids and their vapours. Article 6 contains a synopsis of the principal results of the investigation.

2. "CONTINUOUS MEDIUM" THEORY.

Let K_0 be the value of the dielectric constant when there is a uniform distribution of matter and $K_0 + \delta K$ its actual value at a volume element δv .

In any actual fluid owing to thermal movements, the density at any point undergoes incessant fluctuations and hence the dielectric constant also.

Using Heaviside units, the dielectric displacement $D = K_0 E$ (1) where E is the electric intensity. When the density and consequently the dielectric constant are uniform, there would be no scattering, for the disturbances from different elements of volume would mutually cancel each other, except in the direction of primary propagation.

At a place where the dielectric constant is $K_0 + \delta K$,

$$D_1 = (K_0 + \delta K) E \quad (2)$$

Here, there is a discontinuity of displacement which could be annulled by introducing a supplementary electric intensity

$$E = -\frac{\delta K}{K_0} E \quad (3)$$

For, then

D_1 would become $(K_0 + \delta K)(E - \frac{\delta K}{K_0} E)$ which is equal to $K_0 E$ if we neglect $(\delta K/K_0)^2$ in comparison with unity. As matters actually are, the scattering is identical with the radiation due to a system of electric intensities $-E$ or $\frac{\delta K}{K_0} E$ at the places where the dielectric constant differs from its mean value K_0 by δK .

Suppose we have a volume element δv at the origin of co-ordinates at which the dielectric constant is $K_0 + \delta K$. When the linear dimensions of the element are small in comparison with the wave-length, the amplitude of the disturbance from the element would be proportional to $\frac{\delta K}{K_0} E \delta v$ and hence its energy proportional to

$$\left(\frac{\delta K}{K_0}\right)^2 E^2 (\delta v)^2 \quad (4)$$

As a first step, then, we have to calculate the radiation caused by an extraneous periodic intensity acting throughout a volume element δv at a given point in a homogeneous isotropic dielectric. The problem is analogous to that solved by Hertz in the case of the vibrating electric doublet.

Let E represent the electric intensity

H „ magnetic „

D „ dielectric displacement

and F the extraneous electric intensity acting throughout the element of volume δv

We shall take the magnetic permeability of the medium to be unity.

The field equations are

$$\left. \begin{aligned} \text{Curl } H &= \frac{1}{c} \frac{\partial D}{\partial t} \\ \text{Curl } E &= -\frac{1}{c} \frac{\partial H}{\partial t} \end{aligned} \right\} \quad (5)$$

where c is the velocity of light in vacuo

$$\text{Also} \quad D = K(E + F) \quad (6)$$

$$\text{and} \quad \left. \begin{aligned} \text{div } H &= 0 \\ \text{div } D &= 0 \end{aligned} \right\} \quad (7)$$

Eliminating H from (5) and making use of (6), we get

$$\nabla^2 E - \frac{K}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{K}{c^2} \frac{\partial^2 F}{\partial t^2} + \text{grad div } E \quad (8)$$

To solve (8), following Lorentz,¹⁰ we shall introduce a new vector A given by

$$\nabla^2 A - \frac{K}{c^2} \frac{\partial^2 A}{\partial t^2} = -F \quad (9)$$

In order that (8) and (9) may simultaneously be true,

$$E = \text{grad div } A - \frac{K}{c^2} \frac{\partial^2 A}{\partial t^2} \quad (10)$$

and

$$H = \frac{K}{c} \frac{\partial}{\partial t} [\text{curl } A] \quad (11)$$

Equation (9) is of a well-known form and its solution is

$$A = \frac{1}{4\pi} \int \frac{1}{r} F \left(t - \frac{r}{c} \right) dv \quad (12)$$

¹⁰ H. A. Lorentz—*Les Theories Statistique en Thermodynamique*, pp 42-43.

where the integration is taken over the whole space in which F differs from zero and where $u = \frac{c}{\sqrt{K}}$ is the velocity of electromagnetic waves in the medium, r is the distance from dv of the point at which Δ is required and $F(t - \frac{r}{u})$ is the value of F at time $t - \frac{r}{u}$.

When F is a periodic electric intensity $F_x \cos pt$ in the direction of the z -axis, confined to a single volume element dv at the origin of co-ordinates

$$F_x = 0, \quad F_y = 0 \quad \text{and} \quad F_z = F_x \cos pt$$

Hence from (12)

$$A_x = 0, \quad A_y = 0, \quad A_z = \frac{F_x \delta v}{4\pi u} \cos p \left(t - \frac{r}{u} \right)$$

From (10),

$$E_x = \frac{\partial^2 A_x}{\partial z^2}, \quad E_y = \frac{\partial^2 A_y}{\partial y \partial z}, \quad \text{and} \quad E_z = \frac{\partial^2 A_z}{\partial z^2} - \frac{1}{u^2} \frac{\partial^2 A_z}{\partial t^2}$$

The magnetic intensities, can, if necessary, be easily deduced from (11). For distances from the origin large in comparison with the wave-length,

$\frac{1}{r^2}$ and $\frac{1}{r^3}$ can be neglected in comparison with $\frac{1}{r}$ and hence

$$E_x = -\frac{x}{r^3} \omega, \quad E_y = -\frac{yz}{r^3} \omega, \quad \text{and} \quad E_z = \left(\frac{1}{r} - \frac{z^2}{r^3} \right) \omega \quad (13)$$

$$\text{where } \omega = \frac{p^2 F_x \delta v}{4\pi u^2} \cos p \left(t - \frac{r}{u} \right)$$

The intensity of the radiation would be proportional to $E_x^2 + E_y^2 + E_z^2$ which is given by

$$\frac{p^2 + y^2}{r^4} \omega^2 = \frac{\sin^2 \theta}{r^2} \omega^2 \quad (14)$$

where θ is the angle between the direction of the ray and the axis of z (the direction of the applied electric intensity)

In the case of scattering by a single volume element dv ,

$F_x = -\frac{\delta K}{K} E$ and the ratio of $E_x^2 + E_y^2 + E_z^2$ to E^2 the square of the amplitude of the incident wave is given by

$$\frac{\sin^2 \theta}{r^2} \left(\frac{2\pi}{\lambda_1} \right)^2 \left(\frac{\delta K}{K} \right)^2 \frac{\delta v^2}{16\pi^2} \quad (15)$$

where $2\pi/\lambda_1$ has been substituted for p/u . λ_1 is the wave-length of the incident vibration in the medium.

Let us now consider the scattering produced by the accidental deviations of density in an extended volume. Let us take the X-axis to be the direction of the primary beam. The density deviations would change both in magnitude as well as in position in a perfectly arbitrary manner and there would be no co-ordination of phase between the vibrations scattered by the various elements. As a consequence, over any finite time-interval, the energies and not the amplitudes of the scattered radiations from the different elements of volume would be additive. If $\delta\rho$ denotes the deviation of density from its uniform value ρ_0 in a volume element δv then we can easily show¹¹ by applying Boltzmann's principle of entropy-probability that the mean square of deviation of density is given by

$$(\overline{\delta\rho^2}) = \frac{RT\beta}{N\delta v} \rho_0^2 \quad (16)$$

The relation between density and dielectric constant is given by Lorentz's equation

$$\begin{aligned} \frac{K_0 - 1}{(K_0 + 2)\rho_0} &= \text{constant} \\ \text{Hence } \frac{\partial K}{\partial \rho} &= \frac{(K_0 - 1)(K_0 + 2)}{3\rho_0} \\ \text{and} \\ \delta K &= \frac{\partial K}{\partial \rho} \delta\rho \\ \overline{\delta K^2} &= \frac{(K_0 - 1)^2 (K_0 + 2)^2}{9\rho_0^2} \delta\rho^2 \\ &= \frac{(K_0 - 1)^2 (K_0 + 2)^2}{9} \frac{RT\beta}{N\delta v} \end{aligned}$$

Substituting in (15) $\overline{\delta K^2}$ for δK^2 we get for the ratio of the average intensity of the scattered radiation to that of the incident

$$\frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \frac{\sin^2\theta}{\lambda^2} \delta v$$

and since the radiations from different volume elements are additive

$$\frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \frac{\sin^2\theta}{\lambda^2} \text{ per unit volume} \quad (17)$$

¹¹ Einstein—Ann. der Physik, Vol 1910, p 1275, also C. V. Raman and K. R. Ramanathan—Phil. Mag., Jan 1923.

where λ is the wave-length of the incident vibration in vacuo. The radiation in the direction of the z axis is zero and is a maximum in the xy plane

When the incident light is unpolarised, the ratio of the intensity of the light scattered in a transverse direction to the intensity of the incident beam is given by

$$\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \frac{1}{r^4}$$

In a direction making an angle ϕ with the incident beam, this becomes

$$\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \left\{ \frac{1 + \cos^2 \phi}{2} \right\} \quad (18)$$

To get the extinction co-efficient, we have only to find the total scattering from a stratum of thickness dx and unit area of cross-section. Integrating (18) over the surface of a sphere of radius r , the ratio of the energy scattered by such a stratum to the incident energy is given by

$$\frac{dI}{I_0} = \frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 dx$$

$$\therefore I = I_0 e^{-h}$$

$$\text{where } h = \frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2$$

We might substitute μ^2 for K_0 in the above expressions where μ is the refractive index of the medium for the particular frequency

3. Scattering by Isotropic Molecules.

Considering the problem from a molecular standpoint, the effect of an incident electromagnetic wave on the molecules of a medium is to produce a displacement of the electrons in the molecules which is equivalent to creating an oscillating electric doublet in each molecule

with a period the same as that of the wave. When the molecules are isotropic, the axes of the doublets coincide in direction with that of electric intensity, but when they are anisotropic, the displacements of the electrons are not in general in that direction, but the effect may approximately be taken to be equivalent to creating three doublets with their axes along three principal directions in each molecule. The field to which any molecule is subject is the resultant of that due to the incident wave and that due to the polarisation of the neighbouring molecules. The latter is taken account of in Lorentz's well known treatment of dispersion in homogeneous, isotropic media. In the case of a gas at atmospheric pressure, its effect is negligible. The treatments of the scattering of light by isotropic molecules by the late Lord Rayleigh, Natanson, Sir J. J. Thomson and others do not take into account the influence of the surrounding molecules. Einstein's treatment of the subject does consider the effect due to the polarisation of the surrounding dielectric, but the treatment is non-molecular, and the results apply only to the case of a medium composed of isotropic molecules. With a view to extension to the case when the molecules are anisotropic, a molecular treatment of the problem is given below, taking into account the effect of the neighbouring molecules.

Consider a plane polarised wave travelling in the direction Ox . Let Z be the electric intensity in the wave parallel to Oz and proportional to $\cos pt$. Under the influence of the wave, each molecule becomes equivalent to a doublet with its axis parallel to Oz . Let A be the moment induced in a molecule when it is placed in a field of unit intensity. If the medium be of uniform density and if n_0 denotes the number of molecules per unit volume and M_0 the electric moment of each doublet,

the actual intensity at any point O in the medium is given by

$$Z + \frac{4\pi}{3} n_o M_o$$

and

$$\begin{aligned} M_o &= A \left(Z + \frac{4\pi}{3} n_o M_o \right) \\ &= AZ / \left(1 - \frac{4\pi}{3} n_o A \right) \end{aligned} \quad (19)$$

Now K_o the square of the refractive index of the medium for waves of frequency $\nu/2\pi$ is given by

$$\frac{K_o - 1}{K_o + 2} = \frac{4\pi}{3} n_o A \quad (20)$$

and hence

$$M_o = AZ \left(\frac{K_o + 2}{3} \right) \quad (21)$$

A vibrating electric doublet radiates out energy. According to Hertz's well known solution, the electric intensity at time t at a point, distant (great in comparison with λ) from the doublet is

$$\frac{\nu^2 M_o}{c^2 r} \left(t - \frac{r}{c} \right) \sin \theta \quad (22)$$

where c is the velocity of light in vacuum, θ is the angle between Oz and the direction of the ray and $M_o \left(t - \frac{r}{c} \right)$ stands for the value of the moment at time $t - \frac{r}{c}$

When the molecules of the medium are uniformly distributed and we consider the effect due to a volume whose dimensions are large compared with λ , it vanishes in all directions except in the direction of primary propagation where the secondary waves from the different molecules in the wave-front combine with the original wave and give rise to a plane wave moving with an altered velocity. In any actual fluid medium, however, owing to the thermal movements of the molecules, and the consequent fluctuations of density at any point, there

is a finite radiation of energy in all directions. If n , represents the average number of molecules per unit volume in a volume element δv and $\overline{\delta n^2}$ the mean square of the deviations of that number, then as before

$$\frac{\overline{\delta n^2}}{n_0^2} = \frac{RT\beta}{N\delta v} \quad (23)$$

Consider a volume element δv at O small in comparison with a cubic wave-length, but large compared to the dimensions of a molecule. Let n be the number of molecules per unit volume in δv and let n be equal to $n_0 + \delta n$. The electric intensity at P due to scattering by the molecules contained in δv would be given by

$$\frac{p^2}{c^2} \sin^2 \theta \delta v (Mn - M_0 n_0) \quad (24)$$

where M is the electrical moment appropriate to the density n . When we are considering the average effect over finite intervals of time, the distinction between M and M ($t - \frac{r}{c}$) may be dropped. Now

$$= \frac{p^2}{c^2} \sin^2 \theta \left[(M_0 + \delta M)(n_0 + \delta n) - M_0 n_0 \right] \delta v \quad (24)$$

$$= \frac{p^2}{c^2} \sin^2 \theta (M_0 \delta n + n_0 \delta M) \delta v \quad (25)$$

Now, differentiating (19) and applying (20)

$$\delta M = \frac{(K_0 - 1)(K_0 + 2)}{9} AZ \frac{\delta n}{n_0}$$

$$\begin{aligned} n_0 \delta M + M_0 \delta n &= \left(\frac{K_0 + 2}{3} \right)^2 AZ \frac{\delta n}{n_0} \\ &= \frac{(K_0 - 1)(K_0 + 2)}{12\pi} Z \frac{\delta n}{n_0} \end{aligned} \quad (26)$$

Let us consider the effect due to (25). If E is the electric intensity at P due to radiation from δv , the energy is proportional to E^2 . It is thus

$$\begin{aligned} &\frac{p^4 \sin^4 \theta}{c^4} (M_0 \delta n + n_0 \delta M)^2 \delta v \\ &= \frac{p^4 \sin^4 \theta}{c^4} \frac{(K_0 - 1)^2 (K_0 + 2)^2}{144\pi^2} Z^2 \frac{\delta n^2}{n_0^2} \delta v \end{aligned}$$

Since δn varies from instant to instant according to the laws of chance the average expectation of E^2 over a sufficiently long interval of time is

$$\overline{E^2} = \frac{\rho^4 \sin^2 \theta}{c^4 r^4} \frac{(K_s - 1)^2 (K_s + 2)^2}{144\pi^2} Z^2 \frac{\bar{\delta n}^2}{n_s^2} \delta v^2$$

By (23),

$$\overline{E^2} = \frac{\rho^4 \sin^2 \theta}{c^4 r^4} \frac{(K_s - 1)^2 (K_s + 2)^2}{144\pi^2} Z^2 \frac{RT\beta}{N} \delta v$$

When we consider the effect due to a volume V whose dimensions are large in comparison with λ , the ratio of the square of the electric vector in the scattered radiation to that in the incident is

$$\begin{aligned} \frac{E^2}{Z^2} &= \frac{\rho^4 \sin^2 \theta}{c^4 r^4} \frac{(K_s - 1)^2 (K_s + 2)^2}{144\pi^2} \frac{RT\beta}{N} V \\ &= \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (K_s - 1)^2 (K_s + 2)^2 V \frac{\sin^2 \theta}{r^4} \end{aligned}$$

where λ is the wave-length of the light in vacuo

4. Scattering by Anisotropic Molecules

Let $O'\xi$, $O'\eta$, $O'\zeta$ denote the three principal directions in a molecule whose centre is O'

Let A , B , C be the moments induced in the molecule when placed in a field of unit intensity parallel to $O'\xi$, $O'\eta$, $O'\zeta$ respectively

As before, let Oz be the direction of the incident polarised plane wave and Z the electric intensity along Oz . In a medium composed of isotropic molecules the axis of the induced doublet in each molecule would be parallel to Z , there would be no component along Ox or Oy . In a medium composed of anisotropic molecules, however, there would, in general, be components both along the x and the y axes. But when the axes of the molecules are oriented at random the components of the induced moments along the x and y directions would be as much positive as negative and hence the polarisation fields parallel to the x and y axis

which may be taken as $-\frac{4}{3}\pi n_s \bar{M}_x$ and $\frac{4}{3}\pi n_s \bar{M}_y$ respectively would

vanish. We would however still have $-\frac{4}{3}\pi n_s \bar{M}_z$, because M_z can have only positive values. The effect of the polarisation of the surrounding

molecules is then to produce an additional field of $\frac{4}{3}\pi n, \bar{M}_i$. The resultant electric field at a point in the medium is therefore

$$Z + \frac{4}{3}\pi n, \bar{M}_i \quad (27)$$

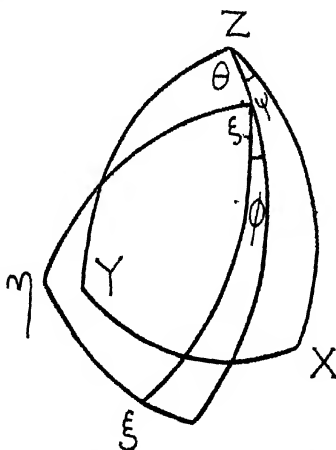
To calculate \bar{M}_i , we note that if the molecules are oriented at random,

$$\begin{aligned} \bar{M}_i &= \frac{A+B+C}{3} \left[Z + \frac{4}{3}\pi n, \bar{M}_i \right] \\ &= \frac{A+B+C}{3} Z \frac{K_s+2}{3} \end{aligned}$$

$$\text{and} \quad \frac{K_s-1}{K_s+2} = \frac{4\pi n_s}{3} \left[\frac{A+B+C}{3} \right] \quad (28)$$

Consider a molecule, the direction of whose principal axes is defined by the Eulerian angles θ, ϕ, ψ ¹

In figure 1, x, y, z represent the points where $O'x, O'y, O'z$ cut a sphere of unit radius, and ξ, η, ζ the points where the axes of the molecule cut the same sphere



The moments induced in the molecule parallel to $O'\xi, O'\eta, O'\zeta$ are

$$\begin{aligned} -AZ \left(\frac{K_s+2}{3} \right) \sin \theta \cos \phi \\ BZ \left(\frac{K_s+2}{3} \right) \sin \theta \sin \phi \\ CZ \left(\frac{K_s+2}{3} \right) \cos \theta \end{aligned} \quad (29)$$

¹ Lord Rayleigh and Sir J. J. Thomson, *loc. cit.*

When these are resolved along Ox , Oy , Oz the components are

$$M_x = Z \left(\frac{K_s + 2}{3} \right) \left[\sin \theta \cos \theta \cos \psi (C - A \cos^2 \phi - B \sin^2 \phi) \right. \\ \left. + (A - B) \sin \theta \sin \psi \sin \phi \cos \phi \right]$$

$$M_y = Z \left(\frac{K_s + 2}{3} \right) \left[\sin \theta \cos \theta \sin \psi (C - A \cos^2 \phi - B \sin^2 \phi) \right. \\ \left. + (A - B) \sin \theta \cos \psi \sin \phi \cos \phi \right]$$

$$M_z = Z \left(\frac{K_s + 2}{3} \right) \left[C \cos^2 \theta + B \sin^2 \theta \sin^2 \phi + A \sin^2 \theta \cos^2 \phi \right] \quad (30)$$

which, for shortness, we may write

$$Z \left(\frac{K_s + 2}{3} \right) L_1, \quad Z \left(\frac{K_s + 2}{3} \right) L_2, \quad Z \left(\frac{K_s + 2}{3} \right) L_3,$$

The mean value of M_x and M_y taken over all orientations is zero, while that of M_z is $Z \left(\frac{K_s + 2}{3} \right) \left(\frac{A+B+C}{3} \right)$. At a point on the y -axis distant r from O , the square of the x -component of the electric intensity due to scattering from a molecule at O is

$$\frac{p^4}{c^4 r^4} M_x^2$$

and from the molecules contained in a volume element δv the average expectation of X'^2 is

$$\overline{X'^2} = \frac{p^4}{c^4 r^4} \overline{M_x^2} n \delta v$$

Since M_x has positive and negative values equally often at random,

$\overline{X'^2}$ is proportional to the number of molecules

Averaged over all orientations of molecules

$$\overline{X'^2} = \frac{p^4}{c^4 r^4} Z^2 \left(\frac{K_s + 2}{3} \right)^2 \frac{1}{15} (A^2 + B^2 + C^2 - AB - BC - CA) n \delta v \\ = \frac{p^4}{c^4 r^4} Z^2 \left(\frac{K_s + 2}{3} \right)^2 f n \delta v$$

where

$$f = \frac{1}{15} (A^2 + B^2 + C^2 - AB - BC - CA)$$

and from a volume V

$$\bar{X}' = \frac{p^*}{c^* r^*} Z^* \left(\frac{K_0 + 2}{3} \right)^* f n \cdot V \quad (31)$$

In the case of the Z -component, we note that it can have only values of the same sign as Z . Hence from a *small* volume element δv , the amplitudes of the electric forces are additive. The Z -component of the electric force due to a single molecule at 0 is given by

$$\frac{p^*}{c^*} M,$$

and from the $n\delta v$ molecules contained in the volume element δv

$$\begin{aligned} Z' &= \frac{p^*}{c^*} M \cdot n\delta v \\ &= \frac{p^*}{c^*} (\bar{M} + \delta M) (n_0 + \delta n) \delta v \\ &= \frac{p^*}{c^*} (M \cdot n_0 + M \cdot \delta n + n_0 \delta \bar{M}) \delta v \end{aligned}$$

The amplitude due to the first term cancels when the effect is taken over a finite volume and as in the case of isotropic molecules, we are left with the second and third terms

$$\begin{aligned} Z' &= \frac{p^*}{c^*} (\bar{M} \cdot \delta n + n_0 \delta \bar{M}) \delta v \\ &= \frac{p^*}{c^*} Z^* \left(\frac{K_0 + 2}{3} \right)^* \frac{1}{L_3} \delta v \cdot \delta n \end{aligned}$$

as in (26).

The mean value of J_3 taken over all orientations is

$$g = \frac{1}{3} (3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA)$$

$$\therefore \bar{Z'} = \frac{p^*}{c^* r^*} Z^* \left(\frac{K_0 + 2}{3} \right)^* \frac{1}{\delta n^2} \delta v \cdot g$$

and by (23)

$$= \frac{p^*}{c^* r^*} Z^* \left(\frac{K_0 + 2}{3} \right)^* \frac{RT\beta}{N} \delta_{11} n_0^* g$$

and from a volume V , the same quantity

$$= \frac{p^*}{c^* r^*} Z^* \left(\frac{K_0 + 2}{3} \right)^* \frac{RT\beta}{N} n_0^* g V \quad (32)$$

and

$$\frac{\overline{X^{11}}}{Z^{11}} = \left(\frac{K_0 + 2}{3} \right)^* \frac{RT\beta}{N} n_0 g = \frac{f}{\gamma g} \quad (33)$$

where

$$\gamma = \left(\frac{K_0 + 2}{3} \right)^* \frac{RT\beta}{N} n_0. \quad (34)$$

When the incident light is unpolarised, the ratio of the weak component to the strong in a direction perpendicular to the incident beam is

$$\frac{2f}{f + \gamma g} \quad (35)$$

For a gas at ordinary pressure obeying Boyle's law, this becomes

$$\frac{2f}{f + g} \quad (36)$$

in accordance with Rayleigh's result.

The total intensity of the scattered light from a unit volume in a direction perpendicular to the incident beam is

$$\frac{p^*}{c^* r^*} Z^* \left(\frac{K_0 + 2}{3} \right)^* \{3f n_0 + \gamma g n_0\} \quad (37)$$

To connect g and f with experimentally determinable quantities, we note that

$$\begin{aligned} f &= \frac{1}{18} (A^2 + B^2 + C^2 - AB - BC - CA) \\ g &= \frac{1}{18} (3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA) \\ g - \frac{1}{3}f &= \frac{1}{9} (A + B + C)^2 \\ &= \frac{9}{16\pi^2 n_0^2} \frac{(K_0 - 1)^2}{(K_0 + 2)^2} \end{aligned} \quad (38)$$

and from (36) in the case of rare vapour for which Boyle's law holds good, the ratio of the weak component to the strong in the transversely scattered light is

$$r_1 = \frac{2f}{f+g} \quad f = \frac{3r_1(g-\frac{1}{3}f)}{6-7r_1} \quad (39)$$

The quantity under the brackets in (37) can be written

$$fn_0(3 + \frac{1}{3}\gamma) + (g - \frac{1}{3}f)n_0\gamma$$

By (39), this reduces to

$$n_0(g - \frac{1}{3}f) \left\{ \gamma + \frac{r_1(9+4\gamma)}{6-7r_1} \right\}$$

and (37) becomes

$$\frac{p^*}{c^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0(g - \frac{1}{3}f) \left\{ \gamma + \frac{r_1(9+4\gamma)}{6-7r_1} \right\}$$

substituting the values of γ and $g - \frac{1}{3}f$ it reduces to

$$\frac{\pi^2 RT\beta}{9N\lambda^4} \frac{Z^2}{r^2} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{Z^2}{r^2} \frac{\pi^2}{n_0\lambda^4} (K_0 - 1)^2 \frac{r_1(9+4\gamma)}{6-7r_1}$$

Since the square of the electric intensity in the incident unpolarised light is $Y^2 + Z^2 = 2Z^2 = I_0$, say, this becomes

$$\frac{I_0}{r^2} \left\{ \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{\pi^2}{2n_0\lambda^4} (K_0 - 1)^2 \frac{r_1(9+4\gamma)}{6-7r_1} \right\} \quad (40)$$

When $A=B=C$, that is, when the molecules are isotropic, $f=0$ and the expression reduces to the Einstein Smoluchowski formula

$$I_0 = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^2} (K_0-1)^2 (K_0+2)^2$$

In the case of a vapour obeying Boyle's law, the expression becomes

$$I_0 = \frac{\pi^2}{2n_0\lambda^2} (K_0-1)^2 \left\{ 1 + \frac{13b_1}{6-7b_1} \right\}$$

The quantity outside the square brackets is the Rayleigh expression for scattering in gases obeying Boyle's law and the multiplying factor is the same as that introduced by Cabannes

To obtain the co-efficient of extinction, we shall first find an expression for the total radiation from a unit volume when the incident light is polarised with its electric vector along the z axis. The squares of the components of the electric intensity in the light scattered from unit volume, in directions perpendicular to Ox , Oy , Oz are (31) and (32)

$$X^2 = Y^2 = \frac{p^2}{c^2} Z^2 \left(\frac{K_0+2}{3} \right)^2 f n_0$$

and

$$\begin{aligned} Z^2 &= \frac{p^2}{c^2} Z^2 \left(\frac{K_0+2}{3} \right)^2 \frac{RT\beta}{N} n_0 \gamma \\ &= \frac{p^2}{c^2} Z^2 \left(\frac{K_0+2}{3} \right)^2 \gamma \gamma n_0 \end{aligned}$$

This can be looked upon as a mixture of unpolarised light equal to $\frac{p^2}{c^2} Z^2 \left(\frac{K_0+2}{3} \right)^2 2f n_0$ and of polarised light

equal to $\frac{\rho^2}{c^2 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 u_0 (\gamma g - f)$ with the vibrations parallel to the z -axis. Integrating over the surface of a sphere of radius r , the total radiation becomes

$$\begin{aligned} & \frac{\rho^2}{c^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 u_0 \left[8\pi f + \frac{8\pi}{3} (\gamma g - f) \right] \\ &= \frac{128\pi^2}{3\lambda^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 u_0 (2f + \gamma g) \end{aligned}$$

Putting in the values of f , g and γ this becomes

$$Z^2 \left\{ \frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^2} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{8\pi^2}{3n_0\lambda^2} (K_0 - 1)^2 \frac{6\mu_1}{6 - 7\mu_1} \right. \\ \left. \left(1 + \frac{2}{3} \gamma \right) \right\}$$

and the fraction of the incident radiation scattered is

$$\begin{aligned} & \frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^2} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{8\pi^2}{3} \frac{(K_0 - 1)^2}{n_0\lambda^2} \frac{6\mu_1}{6 - 7\mu_1} \\ & \left(1 + \frac{2}{3} \gamma \right) \end{aligned} \quad (41)$$

Even if the incident light is unpolarised, the same expression holds good. For a gas obeying Boyle's law, this reduces to

$$\frac{8\pi^2}{3} \frac{(K_0 - 1)^2}{n_0\lambda^2} \frac{\{6 + 3\mu_1\}}{\{6 - 7\mu_1\}} \quad \dots \quad (42)$$

We can easily see that with unpolarised light, since the intensity of the light scattered along the y and z axis is each

$$\frac{\rho^2}{c^2 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 u_0 (3f + \gamma g)$$

and that along the x -axis is

$$\frac{\rho^2}{r^4} N^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0 (2f + 2\gamma g)$$

the distribution of intensity is given by

$$\frac{8\pi^2}{\lambda^4} \frac{I_0}{r^2} \left(\frac{K_0 + 2}{3} \right)^2 n_0 \{ (3f + \gamma g) + (\gamma g - f) \cos^2 \phi \}$$

where ϕ is the angle between the directions of the incident and scattered beams.

When the values of f , g and γ are substituted this becomes

$$\begin{aligned} & \frac{I_0}{r^2} \left[\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 (1 + \cos^2 \phi) \right. \\ & + \frac{\pi^2}{2} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{r_1}{6 - 7r_1} \{ (9 + 4\gamma) + (4\gamma - 3) \cos^2 \phi \} \Big] \\ & = \frac{I_0}{r^2} \left[\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 (1 + \cos^2 \phi) \right. \\ & + \frac{\pi^2}{2} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{r_1}{6 - 7r_1} (4\gamma - 3)(1 + \cos^2 \phi) \\ & + 12 \frac{\pi^2}{2} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{r_1}{6 - 7r_1} \Big] \end{aligned}$$

5. Comparison with Experiment.

We shall calculate the imperfection of polarisation of the transversely scattered light in a number of liquids from (35) and (36) from the corresponding values for their vapours, and compare the results with the values obtained experimentally. For this, we shall use the data

obtained by Rayleigh¹ and by Raman and Seshagiri Rao²
The following table summarises the results.

Substance	WEAK COMPONENT (per cent) STRONG COMPONENT		
	Vapour	Liquid at 3 °C (Calc.)	Liquid at 30 °C (obs.)
Etho.	1.7	20	8.3
Benzene	6.5	75	30.8
CS ₂	12.0	75	70
CHCl ₃	3.0	31	15
CCl ₄	3.1	40	11

The calculated values are uniformly too high. This seems to show that the *hypothesis of random orientations of molecules in liquids, which we have assumed in the development of the theory does not hold good*.

6 Synopsis

1. An electromagnetic theory of the scattering of light in fluids has been worked out without assuming a molecular structure on the basis of Lorentz's treatment of the scattering of light in gases and the Einstein-Smoluchowski formula for scattering derived.

2. The same result is shown to follow if the fluid medium be supposed to be composed of isotropic molecules.

3. The treatment is extended to the case when the molecules are anisotropic in which case it is shown that if the orientations of the molecules are entirely at random, the transversely scattered light is imperfectly polarised, the ratio of the weak component to the strong being

¹ Rayleigh Proc. Roy. Soc. A, loc. cit.

² C. V. Raman and K. Seshagiri Rao Phil. Mag. vol. 45, 1923, p. 625 and
"Molecular Diffraction of Light"

given by

$$I_s = \frac{2f}{f + \gamma g}$$

where $\gamma = \left(\frac{K_0 + 2}{3} \right)^2 \frac{RT\beta}{N} n_0$ and f and g are constants for the molecule. The intensity of the light scattered in a direction making an angle ϕ with the incident beam is shown to be

$$\begin{aligned} \frac{I_s}{r^2} \left[\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 (1 + \cos^2 \phi) \right. \\ \left. + \frac{\pi^2}{2} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{1}{6 - 7\epsilon_1} \right. \\ \left. + 12 \frac{\pi^2}{2} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{1}{6 - 7\epsilon_1} \right] \end{aligned}$$

The expression reduces to the appropriate forms when the medium consists of isotropic molecules and when the medium is a vapour obeying Boyle's law.

The co-efficient of extinction is shown to be

$$\frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{8\pi^2}{3} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{6\epsilon_1}{6 - 7\epsilon_1} \left(1 + \frac{2}{3} \gamma \right)$$

For a vapour obeying Boyle's law, this becomes

$$\frac{8\pi^2}{3} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{6 + 3\epsilon_1}{6 - 7\epsilon_1}$$

4. The observed values of the imperfection of polarisation in liquids are compared with the calculated values and the former are found to be much too small. This seems to indicate that the assumption of random orientation of molecules in liquids is not valid.

I wish to express my best thanks to Prof. C. V. Raman for his kind interest in the work and for his valuable suggestions.

The Scattering of Light by Liquid Droplets, and the Theory of Coronas, Glories and Iridescent Clouds

BY

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1. Introduction.
2. Coronas and iridescent clouds
3. Glories or brocken-bows and their explanation.
4. Intensity and polarisation of the scattered light.
5. Rigorous electromagnetic theory of diffraction by spherical particles.
6. Summary and conclusion

1. Introduction.

A variety of interesting optical effects are known which arise from the scattering of sunlight by droplets of water suspended in the atmosphere and have been discussed by writers on meteorological science. A good account of these phenomena and a discussion of them, on the elementary principles of geometrical optics and wave theory is given in Humphreys' recent book on the "Physics of the Air." The character of the effects depends on the size and number of the droplets, their situation relative to the direction of the sun's rays and the position of the observer. Of these the best known are the coronas seen round the sun or moon when viewed through thin clouds, and the familiar rainbows with their accompanying supernumeraries. Less well-known but not of less interest are the glories or brocken-bows seen when a bank of fog or cloud is viewed by an observer in

a balloon or on a mountain, looking away from the sun, nearly in the direction of propagation of his rays. Finally we have the very beautiful iridescent clouds, which are occasionally seen some 15° to 30° from the sun. The object of the present paper is two-fold, firstly to consider the explanations of these phenomena that have been so far advanced, critically from the standpoint of the electro-magnetic theory of diffraction, and to point out in what respects they are inadequate or erroneous. secondly, to describe the laboratory studies which have been made by the writer of some novel and hitherto unobserved features exhibited by iridescent clouds, and to consider their relation to the meteorological phenomena. A summary of the results obtained is given at the end of the paper

2. *Coronas and Iridescent Clouds*

G. C. Simpson¹ has advanced the very interesting theory that the iridescent borders and irregular patches of colour occasionally shown by thin high clouds some 15° or 30° from the sun or more are only fragments of coronas formed by exceedingly small undercooled droplets of very approximately uniform size. The experimental study of the light scattering by such small droplets accordingly acquires some importance, and it was with a view to investigating the theory of iridescent clouds and other related phenomena that the present work was undertaken. The following experimental arrangement was adopted which is essentially the same as that used by Mecke.² The condensation chamber in which the clouds are observed is a round-bottomed flask, having a diameter of about 18 cm. and containing a little dilute alkali. The flask is connected with two stop-cocks one of which

¹ Q. Jr. Roy. Met. Soc. 38 p. 29

² Ann. der Phys. Vol. 61, 62, 65

opens to the outer air and the other to a vacuum chamber. By momentarily opening the stop-cock connecting the chamber and condensation flask, clouds are formed within the flask by the adiabatic expansion of the air saturated with water vapour. The vacuum chamber is connected with a manometer to note the changes of pressure. By varying this change of pressure, clouds containing particles of any desired size could be obtained. The particles of largest radius obtained were about $8\ \mu$ and the smallest about $1.5\ \mu$.

A 1000 c p. tungsten filament lamp is placed at a considerable distance from the condensing flask, and a beam of light from it focussed by the lens placed in front of it, at the centre of the flask. When the vapours condense, the track of the beam becomes visible as the result of the scattering of the light by the droplets formed. If observations are made in a direction nearly parallel to the direction of light, the eye being placed on the side opposite to that at which the source of light is situated, one can see vivid patches of colour in the track of the beam, red and green being the most prominent tints. If the droplets are large, these coloured patches can only be seen in directions embraced within a small solid angle, but as the size decreases, they become visible at larger and larger angles. The colour of any patch changes as the angle of observation is changed and the track of the beam through the flask shows different colours at the different parts for the same reason, that is, the angle of observation is different at different parts.

Very small particles are obtained with small expansions at a very low pressure. With very thin clouds consisting of small droplets, the coloured patches could be seen even at a large angle (30° — 40°). The observations thus lend an experimental support to Simpson's suggestion about the formation of the iridescent clouds.

When the lens is removed from the arrangement described above and the eye is directed to the source of light through the flask, the coronas may be directly observed when a cloud is formed by expansion. In order that the eye may not be unnecessarily dazzled by the direct light, some opaque obstacle—say the end of the finger may be used to screen it from the direct light. This does not in any way interfere with the observation of the corona. It is found that with smallest droplets the central field is coloured, its tint changing with the size of the droplets; only with larger droplets (larger than about 2μ in the case of water) do normal coronas appear in which the central field is white with a slight-reddish brown edge and surrounded by the usual system of coloured rings. Some measurements were made of the angular diameters of the rings, and the results obtained support Mecke's observation—that except in the case of large droplets, the diameters of the rings show anomalies, the size of the particles as calculated from the simple formula for the different rings showing striking differences.

That the assumptions on which the ordinary theory of coronas is based must fail in the case of very small droplets becomes evident on careful consideration. In the usual treatment the droplets are treated as opaque discs and the problem of finding the diffraction effect due to them is handled with the aid of Babinet's principle. Actually, however, the water droplets are transparent, the rays of light which pass through them emerging as a strongly divergent pencil. If the drops are large, it may be assumed that the rays transmitted in a direction nearly parallel to the direction of the axis have negligible effects. This however is not justifiable in the case of very small drops as the rays passing through the drop and those diffracted at its boundaries or reflected at its outer surface then differ but little in path and hence are capable

of interfering with each other. An attempt has been made by Mecke (*l. c.*) to take account of these complications, and he has obtained a somewhat complex equation for the intensity of the light scattered by the drops. But Mecke's treatment is not satisfactory as he uses elementary methods, the applicability of which in the case of droplets not many times larger than the wave length of light is certainly open to question. The problem evidently calls for a rigorous treatment on the basis of the electromagnetic theory. This is given below in Section 5.

3. *Glories or Brocken-bows and their explanation.*

When favourably situated, one may see rings of coloured light around the shadow of his own head, as cast upon a neighbouring fog bank or cloud. These coloured rings or glories as they are called have been explained in Humphreys' book (*l. c.*) as merely coronas due to the particles near the surface of the cloud scattering light reflected from deeper portions of the cloud, in other words, that the effect is of the same nature as the ordinary corona but due to secondary scattering. This explanation of the brocken-bow has been discussed by Richarz¹ and by Obermayer,² and that it cannot be accepted as correct is definitely shown by experimental observations made with artificial clouds. Using the arrangement described previously, if the eye of the observer be placed on the same side of the cloud chamber as the source and looking down very nearly along the path of the beam passing through it, a succession of colours is seen along its track through the cloud. These colours also change as the angle of observation is changed, and the smaller the particles, the greater is the angle from which they can be

¹ Met. Zeit., 1908, 12 and 14.

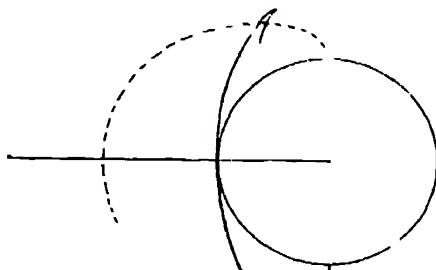
² Met. Zeit., 1912

seen. The complete system of rings is obtained on illuminating the cloud with a beam of sun light and may be viewed in a perpendicular direction with the aid of a plane sheet of glass held at 15° in front of the cloud chamber, so that the observer's head does not screen the cloud chamber from the illuminating pencil. The observations prove clearly that the phenomenon under discussion is shown by every portion of the cloud and therefore really arises from *primary* scattering by the droplets of water.

That the glories or brocken-bows arise in a way which is quite different from that of the ordinary transmission-coronas is proved by the fact that the sequence of colours in the brocken-bows and in the transmission-coronas due to cloud particles of the same size are far from being identical. The normal corona due to large drops shows a central white field with a brownish red margin surrounded by the familiar coloured rings, but in the brocken-bows, the arrangement is different and varies somewhat with the size of the drop. It is sometimes found that just round the central spot (which is the image of the source of light reflected from the first surface of the observing flask) there is a distinct minimum of intensity exhibiting colour, then the intensity increases, the colour being greenish white, bordered by brownish red edge, and then follows the usual succession of coloured rings as in the coronas. It is sometimes found that round the central spot there is a clear maximum and then a belt of minimum intensity and then again a maximum, in other words there is an oscillatory distribution of intensity in the central field. Sometimes it is also observed that in the central field of the brocken-bow only red and green rings or belts are present in different intensities, whitish yellow colour being totally absent, while in the corresponding coronal rings, the central field is yellowish white or nearly without colour.

In order to understand how the glories are formed we have to consider the light which travels back towards the source from the droplets. This arises in two ways, (1) by reflection from the front surface of the droplets, (2) by two reflections and one internal reflection. When a plane wave falls on the spherical particles and is reflected back at its external surface, the reflected wave-front is strongly divergent and as a result, it merely adds a little to the general illumination of the field and does not give rise to any notable diffraction effect. But wave-front (2) formed by internal reflection is not so divergent as (1) and is limited by a cusped-edge, at which it is doubled back. See Fig 1, in which wave-

Fig 1



front (1) is indicated by dotted lines and wave-front (2) by heavy lines. When the droplet is small, the path differences between back and front of the wave near the cusped edge are very small. Hence we may without appreciable error consider the wave-front to be a simple spherical cap of appropriate radius. As a sufficient approximation, we may assume the centre of this spherical cap to be the image of a point, placed on the axis at an infinite distance, produced by two refractions and one reflection. We have now to find in directions making a small angle with the axis back towards the direction of the primary source the aggregate effect of this wave

cap. The problem now is the same as the diffraction produced by a small circular opening in a screen on which light is propagated in spherical waves from a point source. We take as the axis of symmetry the line drawn from the source to the centre of the opening and it is required to find the intensity of illumination at any point P of a plane screen parallel to the plane of the opening and at a distance from the latter. Consider now the position of the wave front of radius a which fills the orifice. Let z be the distance of P from the axis of symmetry and b the distance of the screen from the nearest point or pole of the spherical wave of radius a and then using the usual wave equation, the intensity of illumination at P¹ is proportional to

$$M^2 = \left(\frac{2}{y}\right)^2 (U_1^2 + U_2^2)$$

U_1 and U_2 are calculated by means of Tables of Bessel Functions, where

$$U_1 = \sum (-1)^n \left(\frac{y}{z}\right)^{n+1} J_{n+\frac{1}{2}}(z)$$

$$U_2 = \sum (-1)^n \left(\frac{y}{z}\right)^{n+\frac{1}{2}} J_{n+\frac{1}{2}}(z)$$

$$\frac{1}{2}\psi = \frac{2\pi}{\lambda} \frac{a+b}{2ab} \rho^2 \quad \text{and} \quad \frac{2\pi}{\lambda} \frac{z}{b} \rho = x$$

$$\frac{1}{2}\psi = \frac{1}{2}y \quad \text{and} \quad x = z, \quad \text{where} \quad \rho = r$$

$$r = \text{radius of the orifice}$$

The above series for U_1 and U_2 are used if $z > y$ but in case when $y > z$

$$U_1 + V_1 = \sin \frac{1}{2} \left(y + \frac{z^2}{y} \right)$$

$$-U_2 + V_2 = \cos \frac{1}{2} \left(y + \frac{z^2}{y} \right)$$

¹ For a detailed mathematical treatment of the problem see Gray and Mathews, Chapter XIV, "Diffraction of Light" Also Lommel Abh. D. K. Mayer, Akad. D. Wissensch. XV, 1886.

where

$$V_0 = \sum (-1)^n \left(\frac{z}{y}\right)^{2n} J_{2n}(\cdot)$$

$$V_1 = \sum (-1)^n \left(\frac{z}{y}\right)^{2n+1} J_{2n+1}(\cdot)$$

The maxima and minima values of M^2 are those for which

$$\frac{\partial M^2}{\partial z} = 0$$

The solution clearly gives that the maxima and minima are obtained when either

$$J_1(z) = 0, \text{ or } U_1 = 0$$

Curves for M^2 as ordinate, and Z as abscissa are drawn for

$y = \pi, 1\pi, 5\pi, \text{ and } 9\pi$ (Figs 2, 3, 4, 5)

Fig 2

$y = \pi$

$100M^2$

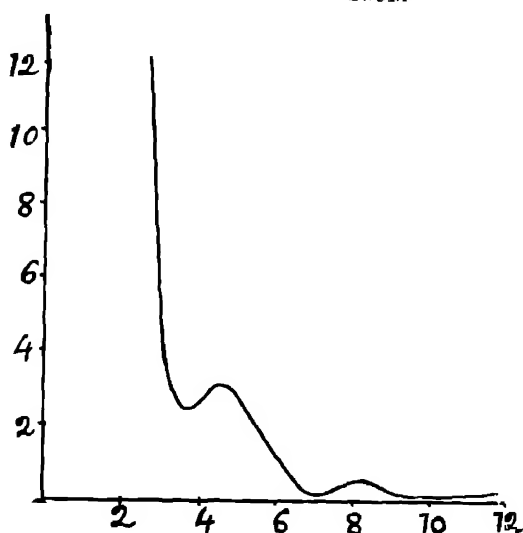


Fig 3

$$y = \frac{1}{2}\pi$$

$$100M^2$$

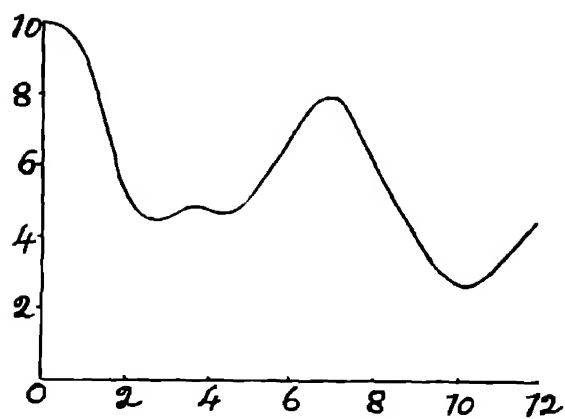


Fig 4

$$y = 5\pi$$

$$100M^2$$

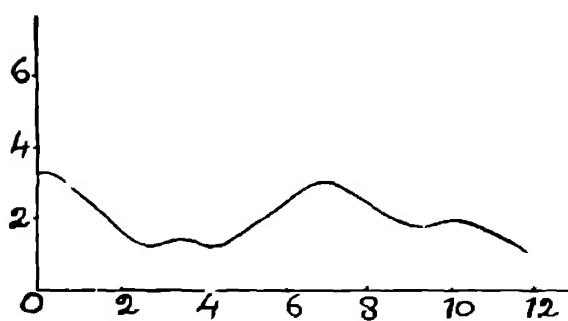


Fig 5

$$y = 9\pi$$

$$1000M^2$$



Curves for $y=\pi$, 5π , and 9π as given in Gray and Mathews (1 c.) and for $y=4\pi$ are drawn, the last showing $M^2=0$ when $z=0$.

From the above expressions it is easily seen that

$$M^2=0, \text{ when } y=n\pi$$

where n may be 1, 2, 3 . . . etc

The curves clearly show the peculiarities of the broken-bow mentioned before. Curves for $y=5\pi$ and 9π show in the central field a belt of minimum intensity round the central spot which is clearly a maximum, showing the oscillatory nature of the intensity in the central field. In the curve $y=4\pi$ (also as it would be in the case of 8π , 12π and so), the central spot is of minimum intensity which only increases from $z=0$ to some higher values of z . These two important peculiarities observed in the central field are clearly explained, the outer rings of the broken bow there showing clear maxima and minima as appears from the curves.¹ Some measurements were made of the position of maximum and minimum in the glory—rings and the results are tabulated below. Considering the experimental difficulties and the assumptions in the theory the results agree fairly well with the observations.

BENZOL

Position of the maximum

y	Observed	Calculated	Observed	Calculated
4π	$5^\circ 4$	$5^\circ 8$	$10^\circ 2$	$10^\circ 8$
5π	$9^\circ 2$	$8^\circ 8$	$11^\circ 5$	$11^\circ 2$
6π	8°	$7^\circ 2$	$11^\circ 1$	$10^\circ 5$

¹ For detailed description of the curves, see Gray & Mathews (loc cit) and also Lommel, loc cit.

WATER

Position of the maximum

	Observed	Calculated	Observed	Calculated
25μ	10.1	9.5		
35μ	7.4	6.0	11.8	12.3
4μ	6.5	5.9	9.8	10.5

Intensities and Polarisation of Scattered Light.

Using a lens to condense the beam of light traversing the flask as in the observation of iridescent clouds, it is noticed that when the eye is moved from $\theta = 180^\circ$ (the direction of the transmitted light) to $\theta = 0^\circ$ (i.e., back towards the source), the intensity of the light at first fluctuates forming coronas as described before, and then becomes very small some-where about 90° . It then increases again at first slowly and then very rapidly at about $\theta = 41^\circ$, which is near the position demanded by the ordinary theory for the primary bow. Particles of size 8μ were produced within the condensing chamber yet no trace of colour could be seen in this direction. This position is indicated by a short maximum. Evidently particles larger than 8μ are responsible for the colours of the rainbow. The intensity of light decreases slightly to increase again as θ is still further decreased; the exact angles are however difficult to indicate and also the intensity does not fluctuate so largely as on the other side. But a slight fluctuation could be noticed. This suggests the formation of supernumeraries. With still further decrease of θ , the glories are formed which are described before. These observations of the sharp maximum at

about 44° are also consistent with the ordinary theory as deduced by Airy, Pernter, Mobius,¹ and others from which it follows that the rainbow bands produced by very small droplets are not only broad, but also feeble, and as their colours necessarily are faint, they frequently are not distinguished, the bow appearing merely white.²

According to the ordinary theory of the rainbow as deduced from wave principles, the supernumeraries should appear, the distance between the maxima decreasing with the increase in size of the droplets. It should be remarked however, that in the solution of the problem it is assumed that the wavefronts are necessarily unlimited or infinite—compared with the wave length of light—on both sides of the inflexion point. This is only valid in the case of very large drops, but as soon as we come to sizes not excessively large in comparison with the wave length of light, the assumed extended character of the wavefronts has no counterpart in reality and Airy's method of treating the problem ceases to be justifiable and a stricter investigation is called for. The theoretical treatment of this problem will be taken up in section 5.

The coronas or iridescent clouds show no trace of polarisation, and indeed the scattered light from $\theta=180^\circ$ to $\theta=45^\circ$ (nearly) is practically unpolarised. At about $\theta=45^\circ$ the light is polarised, the intensity of \parallel' component being greater than that of the \perp' one.³ With further decrease in θ the intensity of \parallel' component decreases and that

¹ Pernter—*Meteorologische Optik*

Mobius—*Ann. der Phys.*, 1910 and 1913

² Humphreys (*l. c.*), page 477

³ The \parallel' component is the component having the vibrations in the plane containing the direction of the incident ray and the direction of observation. The vibration is perpendicular to the direction of observation. The \perp' component, has its vibration perpendicular to the above plane. The vibration is also perpendicular to the direction of observation.

of the other increases, and we reach a neutral point at which the two intensities are equal. The two components are differently coloured, generally red and green, the colour also changing as θ is changed. Beyond this the ratio of the intensity of the two components shows an oscillation with varying θ , the oscillations being most rapid, with the larger particles (3μ or more). With the smaller drops in passing through the smaller values of θ , the colour appears sooner in the two components than with larger drops, otherwise the general appearance is the same. The polarisation of the scattered light is thus practically confined within the region $\theta=0^\circ$ to 45° and its oscillatory character is quite prominent. The difference of colour of the two components is perceived at the largest value of θ within this range when the drops are smallest.

*Rigorous Treatment of Diffraction Problem on the
Electromagnetic Theory.*

Let us suppose that a beam of unpolarised light falls on a spherical obstacle with its centre as the origin and also let the light travel in the negative direction along the axis of z . Suppose we confine our observation to a horizontal plane (*i.e.* plane containing Z , X) at a distance r from the centre, and making an angle θ with the incident beam. If X , Y and Z denote the electric forces parallel to the three axes in the scattered wave, then the vertical component of the scattered light is denoted by Y and the horizontal one by $\frac{rZ - rX}{r}$. Love's solution as corrected and modified by the late Lord Rayleigh¹ gives the following expressions for the two components.

¹ Proc Roy Soc, Vol 84, Ser A, 1910

$$Y = \sum_{n=1}^{n=\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} [M_n \{ \mu P_n' - (n+1) P_n \} + N_n P_n'] e^{ik(ct-r)} \\ \frac{r}{k}$$

$$\frac{xZ - zX}{\gamma} = \sum_{n=1}^{n=\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} [N_n \{ \mu P_n' - n(n+1) P_n \} + M_n P_n'] e^{ik(ct-r)} \\ \frac{r}{k}$$

In these equations, $k = \frac{2\pi}{\lambda}$, λ being the wave length of the incident light, $\mu = \cos \theta$ and P_n or $P_n(\mu)$ is a zonal harmonic of degree n whose axis is the axis of z , Mod Y and Mod $\frac{xZ - zX}{\gamma}$ give the amplitudes of the two components and their squares give the intensities M_n and N_n are functions of the size and optical properties of the spherical particles. The complete expression for N_n is

$$K\psi_{n-1}(\eta) - \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} \right\} \psi_n(\eta) \\ - KE_{n-1}(\eta) + \left\{ K-1 \left(\frac{n}{2n+1} \right) + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} \right\} E_n(\eta)$$

and for M_n

$$\psi_{n-1}(\eta) - \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} \psi_n(\eta) \\ - E_{n-1}(\eta) + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')} E_n(\eta)$$

The expression for M_n is obtained by substituting μ the magnetic permeability instead of K . In optical problems we may take $K=1$ so that the expression for M_n stands as above.

K is the dielectric constant of the material composing the spherical particle, that of the surrounding medium being supposed equal to unity. K may be substituted

for m' where m is the refractive index of the material composing the spheres, relatively to the surrounding medium and $\eta' = m\eta$

$$\psi_n = (-1)^{n-1} 1 \ 3 \ 5 \ 7 \ 9 \quad (2n+1) \left(\frac{1}{\eta} \frac{d}{d\eta} \right)^{n-1} \sin \eta$$

and

$$E_n = (-1)^{n-1} 1 \ 3 \ 5 \ 7 \ 9 \quad (2n+1) \left(\frac{1}{\eta} \frac{d}{d\eta} \right)^{n-1} e^{-i\eta}$$

so that $E_n(\eta) = \Psi_n(\eta) - i \psi_n(\eta)$ where real and imaginary parts are separated

In the case of the water droplets m is taken to be $\frac{4}{3}$ or 1.3333, the surrounding medium being air, $K = \left(\frac{4}{3} \right)^2$

It appears from the above expressions that arithmetical calculations with higher value of η or (ka) are very heavy and tedious, but in order to have an idea about the intensity distribution, calculations have been made with $ka = 12$, a very tedious piece of work so far as the arithmetical computations are concerned

In order to calculate the values of $E_n(\eta)$ the sequence formula was used

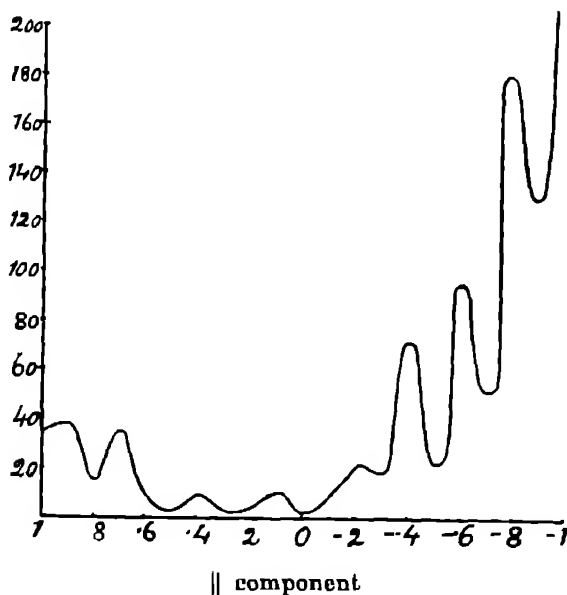
$$E_{n+1} = \frac{(2n+1)(2n+3)}{\eta^2} [E_n - E_{n-1}]$$

starting from E_0 and E_1 . This method is satisfactory as regards the real part of $E_n(\eta)$ but as the imaginary part tends to equality, any error that may creep in is multiplied at the next step by a large factor $(2n+1)(2n+3)$. This difficulty may be overcome in the following manner when the convergence is good. We may calculate the value of ψ_{n+1} and ψ_{n+2} by a straight-forward method very accurately. Having obtained them, we may then use the sequence formula in a reverse direction to find the lower values without any loss of accuracy.

The values of ψ and ϕ were calculated for $ka=12$ and tabulated in table I at the end of the paper. The logarithmic values of M. and N. are tabulated in table II

The quantities $\frac{2n+1}{n(n+1)} \mu P_n' - (2n+1) P_n$ or B. and $\frac{2n+1}{n(n+1)} P_n'$ or A. are functions of η and μ . Their logarithmic values for $\mu = \cos \theta = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 95, 1$, are tabulated and the signs of A. and B. have to be changed properly in obtaining arithmetical values when θ is negative.¹

Fig 6



Curves are drawn in Figs. 6 and 7, representing intensity or

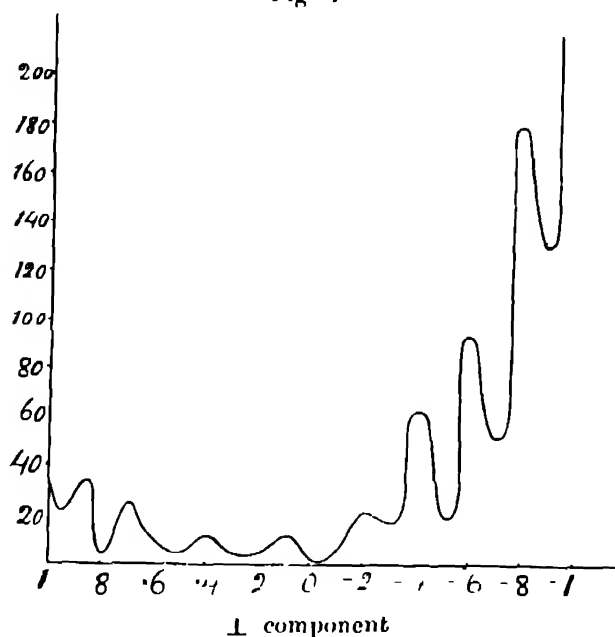
$$(\text{Mod } Y)^2 \text{ and } \left(\text{Mod } \frac{xZ - iX}{i} \right)^2$$

Coronas: It will be seen that in the transmitted direction, the oscillatory character of the intensity of the

¹ Proc. Roy Soc., Vol. 84, 1910

scattered light is most marked, showing sharp maxima and minima. Clearly these are the positions of the

Fig 7



normal coronas, described before. According to the ordinary theory, the positions of the maxima and minima are given by the relation $\sin\theta = \frac{m}{\pi} \frac{\lambda}{r}$. Where these numerical values for the positions of the maxima and minima and compared with those from the rigorous theory (in the case calculated), they are found to differ by 5° to 6° . This discrepancy is to be expected as we have seen before. It is of interest to compare those positions in the case of perfectly conducting particles. Arithmetical calculations for such particles ($ka=9$ and 10) have been made by Proudman, Doodson and Kennedy, (Phil. Trans., A, Vol. 217) on the rigorous electromagnetic theory. The positions for maxima and minima are taken from their paper and when compared with the ordinary theory, are found to agree very well within a few per cent.

Intensity of the scattered light:—When θ decreases, the resultant intensity decreases rapidly till at about 90° it is practically nothing, and sharply increases at 44° , which is near the position of the primary bow. With still further decrease in θ , the intensity fluctuates, showing supernumeraries. Ordinary theory gives the position of the supernumeraries for various sizes of the particle (see Humphreys' book page 476). But for the size we have calculated $ka=12$, the position of the next maximum will be about 8° to 9° from the position of the primary bow, but according to the rigorous calculation it is about 14° - 15° from that position. No such sharp maximum as demanded by the ordinary theory at such a distance could be observed. The intensity of the light slightly diminishes only to rise again. Accurate measurements of the positions of the next maximum could not be made, but the approximate position agrees better with the rigorous theory than with the ordinary one, thus showing the limitations of Airy's theory.

Polarisation of the scattered light:—From the graph drawn, it is found that light is not polarised in the direction of transmission nor is it polarised in the direction $\theta=180^\circ$ to 45° (about). At $\theta=45^\circ$ the polarisation can be detected and the best positions for detecting it lie within the region $\theta=0^\circ$ to 45° . This includes the region where the broken-bow is formed and the rain-bow which is also polarised. These facts agree with what is actually observed experimentally. As a contrast the graphs for conducting particles with $ka=9$ and 10 drawn by Proudmann, Doodson and Kennedy¹ may be referred to. It is found there, that light is only polarised in the directions where the normal coronas are formed and is unpolarised in the directions towards the source. (Just the opposite effect is observed with dielectric particles).

¹ Loc. cit

Summary and Conclusion.

The paper describes experimental and theoretical work dealing with the following optical effects shown by clouds of small liquid droplets (1) coronas (2) glories or brocken-bows (3) white rainbows and (4) polarisation of scattered light.

The following are the principal results

(1) Simpson's theory that iridescent clouds seen at large angles from the sun are really fragments of unusually large coronas formed by exceedingly small droplets receives an experimental verification

(2) The glories or brocken-bows seen when a bank of cloud is viewed by reflected light are shown to be an independent phenomenon due to primary scattering of the sun's rays by the droplets and are not coronas due to secondarily scattered light as has been suggested by some previous writers. They are experimentally found to possess a character different from that of coronas. It is shown that they are due to the integrated effect of the whole wave-front having approximately the form of a spherical cap bounded by a cusped edge emerging after internal reflection at the rear surface of the droplets and the mathematical theory is worked out and shown to be in agreement with experimental results.

(3) The light scattered back nearly in the direction of the source within the region $\theta = 0^\circ$ to $\theta = 45^\circ$ shows remarkable alternations of its state of polarisation in different directions

(4) A rigorous calculation on the basis of the electromagnetic theory shows that the elementary theory of coronas is considerably at fault in the case of very small drops and also that Airy's theory of supernumerary rainbows ceases to be applicable in the case of very small drops. It also explains the effects observed under (3). The theoretical intensity curves show at a glance the relation

between the various phenomena and the rudimentary development of the white rainbow even in the case of such small particles as 1μ in radius

The investigation was carried out in the Palit Laboratory of Physics at the University College of Science, and the author is indebted to Prof. C. V. Raman for his unfailing interest and suggestions during the progress of the work, and especially for his encouragement during the period of tedious arithmetical work involved in the preparation of the paper.

Calcutta, the 23rd July, 1922

TABLE I

n	Ψ	ψ
0	070325	— 044708
1	— 0097117	— 018512
2	— 0083374	0027290
3	00033404	0051628
4	0037938	0010647
5	0023783	— 0028174
6	— 0014056	— 0038550
7	— 0051239	— 0014052
8	— 0065843	0043382
9	— 0032758	012882
10	0091670	023669
11	041736	036181
12	14005	049981
13	41397	064698
14	1 5437	080034
15	7 0485	095747
16	39 100	111654
17	257 04	127609
18	1959 2	143501

TABLE II

n	M_n	N_n
1	1 67700—1 81631 ₁	1 69819—1 67164 ₁
2	1 69021—1 60272 ₁	1 68313—1 80029 ₁
3	1 69040—1 77697 ₁	1 67032—1 51066 ₁
4	1 61610—1 39923 ₁	1 69846—1 67673 ₁
5	1 67701—1 53764 ₁	1 59653—1 28636 ₁
6	1 56442—1 20463 ₁	1 53355—1 13009 ₁
7	2 90520—3 81322 ₁	1 45291—2 94594 ₁
8	1 30900—2 63725 ₁	2 50959—3 01964 ₁
9	—1 33569—2 69340 ₁	—1 41525—2 86341 ₁
10	—1 69896—1 70228 ₁	—1 55601—1 45966 ₁
11	—1 69838—1 67595 ₁	—1 69888—1 70788 ₁
12	—1 69868—1 71434 ₁	—1 49990—1 94811 ₁
13	1 63080—1 38105 ₁	1 53605—1 13602 ₁
14	2 65045—3 30165 ₁	2 75577—3 51296 ₁
15	3 71746—5 57494 ₁	2 00150—4 00300 ₁
16	4 92540—7 85000 ₁	3 85100—5 78216 ₁
17	4 03062—	4 39923
18	5 09800—	5 52403

TABLE for $(\text{Mod } Y)^*$ and $\left(\text{Mod } \frac{xZ-zX}{r} \right)^*$

$\mu = \cos \theta$	$(\text{Mod } Y)^*$	$\left(\text{Mod } \frac{xZ-zX}{r} \right)^*$
1 00	34 1	34 1
0 95	21 2	36 2
0 90	28 9	38 3
0 85	34 3	28 6
0 80	4 8	15 2
0 70	24 7	34 9
0 60	10 1	9 5
0 50	4 8	2 9
0 40	11 2	9 1
0 30	4 4	3 1
0 20	4 9	4 6
0 10	11 2	10 4
0 00	2 1	2 0
-0 10	6 3	7 1
-0 20	20 1	20 3
-0 30	17 5	18 1
-0 40	66 6	68 4
-0 50	20 2	21 1
-0 60	94 6	95 1
-0 70	52 0	50 7
-0 80	179 9	181 4
-0 85	163 6	164 8
-0 90	130 1	132 1
-0 95	280 6	282 1
-1 00	848 6	848 6

III. Earthquake Coda

By

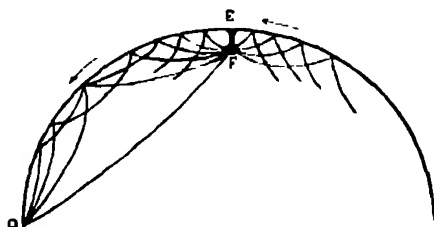
Dr. S. K. BANERJI, D Sc ,

Director, Colaba and Bombay Observatories

No satisfactory explanation has yet been offered for the appearance of the peculiar prolonged disturbance having small amplitudes and somewhat irregular movements which follow the maximal or the long wave phase in the seismogram. The difficulty of identifying this part of the seismogram with the known types of wave propagation has led some seismologists to doubt the existence of Rayleigh waves (see, for instance, Davison's *Seismology*, p. 150, 1921) although the theoretical value of the velocity of propagation of Rayleigh waves has been found to be in close agreement with Klotz's estimate for the mean velocity of the initial long waves. It has been supposed by some that the coda is a local phenomenon and represents merely the subsidiary free vibrations of the earth's surface crust set up by the impulse of the earthquakes and that its nature and duration are largely determined by local conditions. If this view were correct the coda should show smooth decayed vibrations and it is doubtful whether coda could last for hours as it is known to do for distant earthquakes in view of the strong dissipative forces which must influence any free vibrations which the surface crust may take up. Others have maintained that the coda represents the effects of after-shocks only, but this view is again untenable on account of the fact that the effects of after-shocks

should be traceable in all the phases and not simply in the coda. I have recently examined the large number of seismograms collected in the Colaba Observatory and compared them with seismograms from other Observatories. Although I could trace possible local influence and instrumental complications on the entire record, I could not accept the view that the local conditions are mainly instrumental for the production of the coda. The coda presents peculiarities which are different in different earthquakes. It shows a succession of maxima the number and position of which are different in different earthquakes. It is on the whole periodic and sinusoidal (about 12 seconds) and in this respect it presents a striking resemblance to the long wave phase. In view of this similarity one is disposed to think that the coda and the long-wave phase have a common origin. It seems to me that the whole question is bound up with the mode of production of Rayleigh waves. It has been suggested that the long waves are those distortional waves which suffer innumerable reflections at the surface and, as it were, creep round beneath the surface as in the case of the whispering gallery phenomenon. But whether this mode of creeping of waves beneath the surface constitutes an essentially different phenomenon from the so-called Rayleigh waves remains to be seen. On the other hand the identification of the long wave phase with the Rayleigh waves gives such a satisfactory explanation both as regards the unusually high preponderance of this phase and the velocity of propagation that no scientist should lightly discard Rayleigh waves simply because he has not been able to explain the coda. Suppose we consider the disturbance originating from a finite earthquake focus having an average depth of 10 Km. Initially only irrotational and equivoluminal waves will be generated but no Rayleigh waves. If the force at the focus be a succession of

impulses or consists of a series of shocks and also after-shocks, then a succession of these waves will be generated. The Rayleigh waves being two-dimensional disturbances will require a two-dimensional source for their production and it is precisely when the irrotational and equivoluminal waves reach the epicentral tract that this region acts as a secondary source of disturbance for the production of Rayleigh waves



In the figure, F is the focus, E the epicentre and O the observer. Once it is recognised that a part of the energy emanating from the focus F and carried away in the form of irrotational and the equivoluminal waves is capable of being transformed into Rayleigh waves on these waves reaching the surface, no difficulty is experienced in explaining the coda. For there is no reason why this process of transformation should be confined to the epicentral region alone, although no doubt the largest effects will be produced there which will mainly account for the maximal phase in the seismogram. The body waves will be propagated in all directions from the focus. Those reaching the surface between the epicentre and the observer (minor arc) will be partly reflected into waves of the original type and into *wechselwellen* and partly transformed into Rayleigh waves. The Rayleigh waves so formed will reach the observer earlier than those produced in the epicentral tract and consequently will be mixed up with the distortional waves and shown in the S phase. On the other hand those waves which reach the surface on the

side of the epicentre away from the observer (major arc) will be similarly partly reflected and partly transformed into Rayleigh waves, the latter propagating in all directions over the surface. These Rayleigh waves after passing through the epicentral tract will evidently reach the observer later than those generated in the epicentral tract and consequently give rise to the coda in the seismogram.

METEOROLOGICAL OFFICE, SIMLA.

July 28, 1922.

IV. On the Chronographic Determination of Acceleration of Gravity

By

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Introduction

In his well-known investigations with the phonodeik, D C. Miller¹ used a chronographic fork giving a very brief flash of light through slits attached to its prongs once in each oscillation which was registered on the moving photographic film and served as a standard against which the frequencies of sounds recorded on the film could be determined. A similar device has been employed for oscillographic determination of frequencies in instruments constructed by the General Electrical Company.² The merit of the arrangement lies in the sharpness of the lines representing the successive flashes on the film which permits the measurement of their relative positions to a high degree of accuracy and so surpasses, for all quantitative purposes, the method of recording the vibrations of a tuning fork on a smoked paper ordinarily used in chronographic work. Various types of instrument³ have been developed using the chronographic or fall plate method for the determination of the acceleration of gravity, but all of them

¹ D C Miller, " Science of Musical Sounds, Macmillan, 1914.

² Journal of the Franklin Institute, 1922.

³ Of Brown's or Edelmann's apparatus, School Science and Mathematics VIII, p. 387, 1906.

suffer from the common defects—in that (i) the resistance offered by the smoked plate to the style of the recording fork is uncertain and (ii) the computation of distances of fall from the wavy nature of the records is liable to much uncertainty—and so there are, in fact, serious drawbacks in all quantitative determinations of the constant from measurements of time and the corresponding distances of fall

In the following investigation the acceleration of gravity was determined by dropping a photographic plate on which chronographic flashes were recorded by an electrically-maintained tuning fork as in D C Miller's work, the frequency of the fork being simultaneously determined by direct comparison against a standard clock by the method of the sub-synchronous pendulum' developed at Calcutta

Theory of the Method

The vertical distances of fall of a body from the point of rest being represented by $S_1, S_2, S_3 \dots$ and the corresponding times of fall by $t, t+T, t+2T \dots$ where T is a constant such as the period of a fork, the following equations connect the distances of fall and time with the initial velocity (u), if any, of the body and the acceleration of gravity acceleration at the place.

$$S_1 = ut + \frac{1}{2}gt^2 \quad \dots \quad (1)$$

$$S_2 = u(t+T) + \frac{1}{2}g(t+T)^2 \quad \dots \quad (2)$$

$$S_3 = u(t+2T) + \frac{1}{2}g(t+2T)^2 \quad \dots \quad (3)$$

¹ For fuller information vide Prof C V. Raman and A Dey, Proc Roy. Soc, Vol. 95, 1919, also Durgadas Banerji, Proc I A C S, Vol VII, Parts III & IV

Eliminating u and t from the above equations

$$g = \frac{S_1 - S_2 - S_2 - S_1}{T^2}$$

$$= n^2 [S_1 - \bar{S}_2 - S_1 - S_1] \quad (1)$$

Where n = frequency of the fork, and $S_1 - S_2$ and $S_2 - S_1$ measure the distances of fall in two successive periods of the fork. The equation (1) being true only for vacuum, a correction term due to frequency is required to be added to (1) for fall under atmospheric or reduced pressure given by

$$+ \frac{V \times 0.001298}{M(1 + 0.00367t)} \frac{B}{760}$$

where V is the volume and M the mass of the falling body B and t the pressure and temperature of the air respectively. The viscous drag on the falling body which is independent of pressure but depends on the velocity is not such as to affect the results seriously in the *initial* stages of fall of a heavy body, and the corresponding correction may be left out of account specially in work under reduced pressure.

Apparatus and Experimental Procedure and Results.

Sunlight falling on a rectangular horizontal slit is focused by a lens on a pair of fine horizontal slits -- forming a stroboscopic arrangement-- attached to the prongs of a tuning fork (frequency 60/sec), so that, when the fork is not vibrating, a well-defined horizontal slit of light diverges out from the back of the slits. The stroboscopic slits may be made by fixing in juxtaposition the sharp edges of cut Gillete-razor blades so as to leave a slit of 1/5th mm. width

in metal plates rigidly fixed on to the prongs of the fork. The light passing through the slits is focussed by another lens through a glass-window in a vertically fixed cast-iron pipe in which the photographic plate could be dropped by electromagnetic release in a vertical plane containing the point of focussed light. The pipe is closed below and might be evacuated through an air pump connection below after closing the top with a ground glass lid fitted airtight by a paste^{*} of rubber grease and paraffin. A wooden lid of the pipe fixed below the glass lid holds an electromagnet which could be operated from an outside switch and from which is hung, in bifilar suspension of strings, a rectangular slide constructed so as to hold in vertical position a half sized photographic plate just above the point of focussed light in the same vertical plane with it. The exact verticality of the hanging slide was ensured by attaching counterweights on the back-side of the slide. The slide after being loaded and tested for verticality could be enclosed in a paper cover which is taken out after hanging it in position in the tube.

The procedure adopted in measuring the frequency of the fork accurately is to run in maintained oscillation a 100 cm iron rod pendulum by an electromagnet in series with the interrupted current of the fork. The pendulum being hung in front of the standard laboratory clock, determinations of its frequency could be made each time before and after a record is taken, by noting the coincidence period—for the same phase of motion—of the reflection of a bright source from the mercury bob of the clock pendulum and the shadow of the sub-synchronous pendulum rod cast on a tissue paper scale fixed so as to have the two amplitudes on it equal. The reflection of the slit of light being focussed on the tissue paper by a lens,

^{*} A suitable paste is made by mixing together 20 parts of India rubber, 10 parts of grease and 4 parts of hard paraffin over a slow fire.

computations of the coincidence period could be made to within a fifth of a second. Calculations of the frequency of the fork are made from the relation $n = mN$ where m is the constant frequency ratio (an even integer), and N the calculated frequency of the sub-synchronous pendulum estimated to have an accuracy of 100,000.

In the measurement of the distances of the sharp edges of the records on the Adam Hilger comparator microscope reading to a thousandth part of a mm., the possible sources of error were the discrepancies due to random and systematic errors of setting the cross wire on the edges of the mark and were sensibly minimised by taking a large number of settings on parallel lines near enough and taking the mean. The frilling of gelatine on the photographic plate was not such as to affect the readings to the third place of decimals.

TABLE I

Serial No	n^1	$s_1 + s_2 - 2s_1 \times 10^1$	Calculated apparent g	Buoyancy correction.	Corrected g	Remarks
1	3027 661	3232	978 54	0 23	978 77	Plates under atmospheric pressure
2	3027 508	3232	978 51	0 23	978 74	
3	3027 661	3232	978 54	0 23	978 77	
4	3026 415	3233	978 44	0 23	978 67	
5	3026 601	3233	978 50	0 23	978 73	
6	2956 858	3309	978 42	0 23	978 65	
7	2019 782	3352	978 71	0 05	978 76	Plates under pressures 15 to 20 cms
8	2019 249	3353	978 72	0 05	978 77	
9	2020 754	3351	978 74	0 05	978 79	
10	2019 782	3352	978 71	0 05	978 77	

Table I gives a few typical measurements from plates for fall with air under the atmospheric pressure and when

reduced to 15-20 cms of mercury by a hand pump. The accepted value of g for Calcutta being 978.76, the results obtained are fairly correct to the first place of decimals. It will be noted that though the buoyancy correction has been reduced considerably under diminished pressure, the viscous drag on the falling plate is not such as to affect the results to the first place of decimals, in pressures of air considerably reduced. It is hoped to continue the work in much higher stages of vacuum when a suitable opportunity arises.

In conclusion, I have to express my best thanks to Prof. C. V. Raman, for the great interest he took in the work.

University College of Science,
Calcutta

Plate I

Fig 1



Fig 2



Fig 3



Fig 4



Fig 5

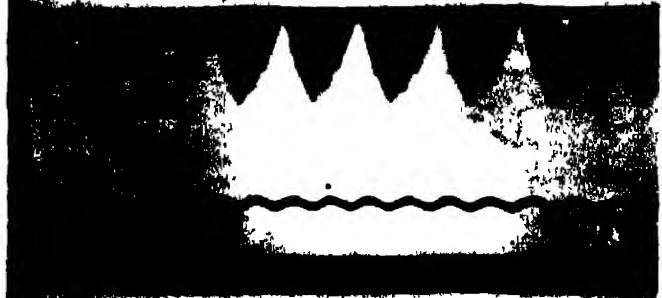


Fig 6



Fig 7



OSCILLATIONS OF SPHEROIDAL DROPS AND PHENOMENA OF SPHEROIDAL STATE

V. On the Oscillations of Spheroidal Drops and the Phenomena of the Spheroidal State.

By

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[Plate I]

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1. Introduction.
2. Experimental arrangements and observations
3. Theory.

SYNOPSIS AND CONCLUSION

PART I.—THE OSCILLATIONS OF SPHEROIDAL DROPS

1 Introduction.

It is well known that when the upper surface of a vibrating plate is covered with a layer of mobile liquid, the surface usually presents a beautifully crisped appearance. A full account of experiments on this

subject was given by Faraday in the Philosophical Transactions of the Royal Society, 1831. Another series of beautiful forms are observed when, instead of a layer of liquid, we take a drop which does not wet the surface and rests on it in the form of a spheroid. These seem to have been first observed by C W Batdorf¹. In the present note an account is given of the quantitative study of the vibrating drops. The natural frequency of oscillation has been investigated, and it has been found that the amplitude of motion must be taken into consideration in deducing the frequency. The relation between the vertical motion of the support and the horizontal oscillation of the drop has been determined. It has been found that the maintenance falls under the class of those under forces of double frequency as in the cases discussed by Faraday where the motion of the liquid surface is vertical.

2. *Experimental Details*

In order to study the oscillation of the drops Prof C V. Raman's Motor Vibrator² was used with a slight modification. The rocking lever was made to vibrate in a vertical direction. Attached to this was a watch-glass which was capable of sliding along the rod and of being fixed in any desired position, large variations of its amplitude of motion could be made by shifting the crank pin along the slot (see p 447, Physical Review, Nov. 1919), and finer adjustments of amplitude were made by moving the watch-glass along the vibrating lever. The frequency of oscillation was kept constant by a sliding rheostat, and a stroboscopic fork. The frequency was kept constant at about 60 oscillations per second, and clean mercury drops were used.

¹ C W Batdorf, Physical Review, Dec. 1912

² Prof C V Raman, Physical Review, Nov. 1919

In order to measure the diameter and the amplitude of vibration of the drop, the following arrangement was made. Light from an arc lamp was reflected through the bottom of the watch-glass, and by means of a right-angled prism, an enlarged picture was obtained on a white screen by a good lens. This arrangement is suitable for showing the phenomena to a large audience, and for photography.

When the support oscillates up and down, the drop takes the form of a peaked star, the number of star-points depending upon the frequency of vertical oscillation, and on the dimensions of the drop. The crests and troughs of the marginal wave succeed each other so quickly, that we cannot detect the different phases of the motion. Hence we observe double the number of star-points actually present. By changing the dimensions of the drop, the number of star-points may be increased, the frequency of vertical oscillation being kept constant.

Plate I shows some of the star-figures obtained. Fig (1) represents a two-point star, photographed as a four-point one. The circular figure of equilibrium assumes an elliptical shape. The vibrating part of the drop is easily recognised by the half-shaded portion. A figure (not reproduced) shows a three-point star, the shape of the disturbed figure being an equilateral triangle. Fig (2) shows a four-point star, the disturbed figure being a square. Figs. (3) and (4) show five- and six-point stars in which the disturbed figures are a pentagon and hexagon respectively.

3. *Determination of the frequency of the star-points.*

To find out whether there was any definite relation between the frequency of vibration of the star-points, and that of the vertical oscillation for different cases, an electromagnetic vibrator was brought in unison with

the vertical oscillation, and its movement and that of the vibrating star-point, were simultaneously photographed as wavy curves. Figs. 5 and 6 show simultaneous records, from which it is evident that the frequency of vibration of the star-point is half that of the vertical oscillation. In this way, when by varying the diameter of the drop the number of star-points was changed, it was observed that the above relation remained true. It was also noticed that the motion of the star points was not symmetrical and simple. The nodal points also were not places of absolute rest, but a slight regular motion was perceptible.

4 *Calculation of the natural frequency of oscillation of the star-points.*

The motion of the star-points is practically confined to two dimensions, and then the calculation becomes very simple by Rayleigh's method of energy. Let us represent the radius vector at any instant in the form

$$r = a_0 + \sum_1^n a_n \cos n \phi \quad (1)$$

The potential energy due to capillarity from the configuration of equilibrium is given by

$$V = \frac{1}{2} \pi T (n^2 - 1) a_n^2 a \quad (2)$$

where a = radius of the drop

T = surface tension

n = number of the star points

The velocity potential of the liquid motion is given by

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} = 0$$

$$\therefore \psi = A r^n \cos n \phi \quad (3)$$

where Λ is determined from the condition

$$\frac{\partial \psi}{\partial r} = \frac{\partial r}{\partial t} \text{ when } r = a$$

The kinetic energy is by Green's theorem

$$\begin{aligned} T &= \frac{1}{2} \rho \int \left\{ \psi \frac{\partial \psi}{\partial r} \right\}_{r=a} d\phi \\ &= \frac{1}{2} \rho \Lambda^2 \pi a^3 \end{aligned}$$

On putting the value of Λ we obtain

$$T = \frac{1}{2} \rho \left(\frac{\partial a_n}{\partial t} \right)^2 \frac{a^3}{n} \quad (4)$$

From (2) and (4) the frequency N is calculated and found to be given by

$$4\pi^2 N^2 = T_n \frac{(n^2 - 1)}{\rho a^3} \quad (5)$$

Formula (5) is only true when the amplitude of motion of the star points is small. Dr Bohr¹ has given a formula when the amplitude of motion is finite and not infinitesimal. His formula is given by

$$4\pi^2 N^2 = q^2 \left\{ 1 - \frac{a_n^2}{16a^2} \frac{(n^2 - 1)(34n^2 - 33n^2 + 50n - 18)}{(2n^2 + 1)(2n - 1)} \right\} \quad (6)$$

where $q = T_n \frac{(n^2 - 1)}{\rho a^3}$ approximately

From (5) and (6) it is evident that the effect of the finite amplitude of motion is to diminish the natural frequency. Table I shows a comparison of the calculated frequencies from formulæ (5) and (6) respectively.

TABLE 1

Mercury Drops

Frequency of the vertical oscillation 60 per second

Number of star points	Diameter cm	Amplitude cm	Calculated frequency from (5)	Calculated frequency from (6)	Observed frequency
3	51	08	37	29.6	30
4	71	07	36	31.0	30
5	1.0	05	31	29.1	30
6	1.08	08	36	29.1	30
7	1.32	07	34	30.0	30
8	1.42	08	37	30.0	30
9	1.49	08	41	32.0	30

The frequency of the star-points should be about 30 per second, and from the table it is evident that the calculated values for formula (5) are much greater than the observed values, while formula (6) agrees well with them.

5. *Maintenance of vibration of star-points.*

The up and down motion of the support disturbs the figure of equilibrium of the drop. The simplest disturbed figure from a circle is an ellipse. This means that when there is contraction of the circular boundary in one direction, there is extension in another, and *vice versa*. As the support is moving upward, let us suppose that the liquid is also moving away from the centre of drop in a horizontal direction. At the instant when the

support is at the extremity of its upward journey, the liquid still moves outward on account of its inertia, stopping when the support is at the extremity of its downward journey. At this instant the restoring force is very large, and as the support moves upward, the liquid moves inward; this inward motion comes to an end when the support is at the extremity of its downward journey. This outward and inward motion of the liquid shows up as star-points. It is now clear from the nature of the motion of the star-points that the period of oscillation is double that of the support. It is also evident that the motion cannot be symmetrical since the inward motion is to some extent resisted, hence the oscillation curve of the star-point, see Figs 5 and 6, is asymmetrical. The curve also shows presence of harmonics.

PART II—THE PHENOMENA OF THE SPHEROIDAL STATE

1 *Introduction*

The phenomena of the spheroidal state of water engrossed the attention of the early physicists whose first object was to establish whether the drop of water touched the surface of the hot plate or not. This being settled, the question arose as to how the drop is enabled to float on a cushion of its own vapour. In 1878, Johnstone Stoney¹ put forward the theory of polarised stress arising from the difference of temperature of the small gap on its two surfaces. His expression for the stress S is given by

$$\frac{Q'}{PT}$$

where Q represents the heat conducted across the gap per second, P is the vapour pressure, and T the absolute temperature of the gap. Q can be calculated if the width of the gap, its area, and the thermal conductivity are

¹ British Assoc. Report, 1878

known. Hence if Stoney's theory be correct, the width of the gap at different temperatures of the hot plate must be capable of calculation¹ With a view to test this, the investigation of the theory of the spheroidal state was undertaken at the suggestion of Dr. Raman. The experiments resulted in establishing a definite relation between the width of the gap and the difference of temperature between the hot plate and the drop, and some interesting facts were also noted concerning the gap and the star-form oscillation of the spheroidal drop.

2. *Experimental arrangements.*

A simple arrangement was made for the observation of the gap. The drop rested on a polished convex plate of silver which was heated by a Bunsen burner, and is anchored by a fine wire held above it, to which the drop sticks without interfering with the phenomena at all. A powerful beam of light from an arc-lamp passes through the narrow gap between the drop and the plate, and a magnified image of the gap is focussed by a camera lens on a screen where its behaviour can be observed. All superfluous light can be cut off by suitable screens placed behind the drop. The temperature of the hot plate was noted by a thermo-couple soldered to it. The temperature of the drop almost remains constant at 95.6°C as has been shown by Batdorf,² hence the difference of temperature between the hot plate and the drop was simply obtained by noting the temperature of the hot plate, and subtracting 96°C from it.

In order to study the variation of the width of the gap with temperature, the mass of the drop was kept constant by keeping the size of the image the same on

¹ See also Maxwell's expression for the polarized stress, Phil. Trans., 1870, p 252

² Physical Review, Dec 1912

the screen. Careful measurements of the gap at various temperatures were taken, and a table was drawn up. It was found that the width of the gap was definite at a fixed temperature of the hot plate when the size of the drop was the same. Table I shows the widths of the gap at various temperature differences D .

TABLE I

Size of drop kept constant at $r = 7.5$ mm

No	h in mm	$D^{\circ}C$
1	1.25	224
2	1.10	304
3	1.60	490
4	1.50	364
5	1.10	304
6	1.25	224
7	.75	104

In the course of these experiments, it was observed that a fine droplet when thrown upon the hot plate began to jump like an elastic ball. This led to the enquiry if the spheroidal drop actually oscillates up and down in a vertical plane. This point was ascertained by photographing the gap on a moving plate. The various phases of the gap were at once evident from the picture. It was found that the gap was not stationary, but opened and closed periodically. The rate of the periodic opening and closing of the gap depends in a compound manner upon the difference of temperature between the hot plate and drop and the size of the drop. Fig 7 in Plate I illustrates the periodic closing and opening of the gap,

the simultaneous record of a style attached to an electrically maintained fork making 60 vibrations per second indicating the frequency of the motion. Since the hot plate is stationary, the closing and opening of the gap must be due to the vertical oscillation of the drop, the frequency of the latter being the same as that of the closing and opening of the gap. The asymmetrical character of the vertical oscillation of the drop is clear from the figure where the white space (when light passes freely through the gap) has a greater width than the dark space, *i.e.*, phase of obstruction to light.

It was found, however, that there are in fact two types of the spheroidal state. (1) In the first type (100° difference of temperature, more or less), the drop is stationary, no oscillation takes place, nor is any ripple motion observed on the surface of the drop, though convection currents may be visible. (2) At about 200° difference of temperature the drop begins to oscillate up and down, resulting in periodic closing and opening of the gap. Fine ripples appear on the surface, and vigorous motion of the drop sets in, sometimes the drop takes the form of an elongated spheroid, moving bodily from place to place. If this motion is stopped the drop takes a star-shaped form. Batdorf has given a complete study of these star-forms. The peaks of these star-forms vibrate in the horizontal plane, but on account of the persistence of vision the drop appears stationary. Stroboscopic observation renders the oscillation apparent. The number of these star-points, *i.e.*, the peaks observed is double the number that is actually present. The number of these star-points depends upon the temperature difference and the size of the drop. It was found that by slightly moving the burner, and thus decreasing the temperature, the peaks begin to decrease in magnitude, and then suddenly another pattern starts up, the size of the drop

remaining almost the same. If we keep the temperature constant, we obtain a series of forms in which the star-points diminish in number, as the size goes on diminishing by escape of vapour from the gap and evaporation. For the success of these experiments, distilled water should be employed, and the plate must always be clean and polished. To start the star-forms, sometimes slight coaxing is necessary. As soon as the body-motion of the drop sets in, it must be concluded that the drop will soon take up the star-form. By employing a shallow plate and a large drop, big star-forms are obtained.

3. *Theory of Spheroidal State*

A relation between D and h can be obtained on the assumption that the whole quantity of steam formed per second escapes from the gap according to the laws of viscosity, and that the radial velocity of steam is zero at the surface of the hot plate and at the bottom of the drop. With these premises, we have the quantity M of steam escaping per second

$$M = \frac{h^3 P}{6\mu} \rho \quad (7)$$

where P denotes the excess of pressure within the gap over the outside, ρ is the density and μ the viscosity of the steam. The heat conducted across the gap per second is given by

$$Q = \frac{KD}{h} \pi a^2 \quad \dots \quad (8)$$

where K represents conductivity, and a the radius of the drop. Hence the quantity of steam formed per second is equal to

$$M = \frac{KD}{hL} \pi a^2 \quad (9)$$

L = latent heat of steam,

Equating (3) and (5) we have

$$h' = 11 \left[\frac{6\mu K \pi a^2}{11 D^2 \rho} \right] \quad (10)$$

Equation (10) which is dimensionally correct shows that h is proportional to D if the term in the bracket remains constant. For the same size of the drop, the term in the bracket is almost a constant; from the observed values of h and D for a given size of the drop given in Table I, a graph was drawn with h' as ordinate and D as abscissa. The curve is found to be accurately a straight line. Hence the difference of temperature between the hot plate and the drop is directly proportional to the fourth power of the width of the gap. The absolute value of h can be calculated from (10) by assuming that the pressure inside is greater than outside, such that $P - \pi a^2$ is equal to the weight of the drop. The calculated value of h comes out a little higher, probably on account of the uncertain values of the constants in the circumstances, and moreover there is always evaporation at the surface. At any rate, we can regard equation (10) to be approximately true.

We have seen that the spheroidal drop oscillates vertically, the formation of the star-forms with vibrating peaks can now be explained in terms of the vertical oscillation. Let us recall the behaviour of a drop of mercury resting on a watch-glass made to oscillate vertically discussed in Part I of the paper. The drop takes the form of a star with vibrating peaks. The frequency N of these peaks vibrating in the horizontal plane, must be half that of the vertical oscillation N' , therefore

$$N = N'/2 \quad (11)$$

and the number n of the peaked points is determined by

$$n^2 - n + \pi^2 N^2 a^2 \rho / T_s = 0 \quad (12)$$

where T is the capillary tension, ρ the density and a the radius of the drop

Table II has been drawn up from (11) and (12) showing the values of N , σ and n the number of peaked points.

TABLE II
Water Drops

No	N	σ cm	n
1	50	74	4
2	100	72	5
3	300	63	6
4	50	42	3
5	100	57	4
6	300	51	5
7	300	30	3

It is observed from (1), (2) and (3) that for about the same size of the drop when the frequency of vertical oscillation is increased two times and three times, the number of peaked points increases from four to five and five to six respectively. For the same value of N , when the size of the drop is halved, the number of peaks is also halved, as shown by (3) and (7). The number of peaks is approximately proportional to the size of the drop when N remains the same

Just as mercury drops are thrown into vibrating star forms by a vertical motion of the support, the same effect occurs in the case of spheroidal drops of water. On account of the vertical oscillation, the drop takes the form of a vibrating star. The frequency of these vibrating peaks being always half that of the vertical oscillation,

the number of the star-points is determined by the size of the drop. For a given size of the drop, when the temperature rises, the rate of vertical oscillation N increases, so also the number of star-points, as shown in Table II, and remarked above in the preceding paragraph. When the temperature remains the same, and the rate of vertical oscillation remains constant, the frequency of the star-points has the same value, but the number of star-points increases with increasing size of the drop. But when the size of the drop is increased to such an extent as to change the rate of vertical oscillation, the resulting change in the number of star-points is a complicated one and cannot be calculated from (12) as N is indeterminate, *i.e.*, the function upon which N depends in the case of spheroidal drops of water, is unknown.

The number of star-points is always an integer. Hence, when it so happens that the size of the drop is such that equation (12) is not satisfied with n an integer, fine ripples appear upon the surface, vigorous motion sets in, till the size changes by evaporation and escape of steam from the gap, and equation (12) is satisfied. Then the star-form begins at once. These ripples and body motion of the drop are also observed in the case of mercury drops oscillating vertically when (12) is not satisfied.

SYNOPSIS AND CONCLUSION.

Part I of the paper discusses the theory of the star-form oscillations of mercury drops resting upon a vertically oscillating glass plate. It is shown that the frequency of horizontal oscillation is half that of the vertical oscillation. The presence of harmonics whose frequency is $\sqrt{2}$ times that of the vertical movement is also noticed. It is shown that the large amplitudes of motion maintained in practice have a very sensible

influence on the natural frequency of the drop and must be allowed for, and that they also result in a distinct asymmetry in the oscillations

Part II discusses the theory of the spheroidal state. It is shown that there are two types of spheroidal state, one in which the gap between the drop and the hot plate is stationary, and the second type in which the gap opens and closes periodically. The second generally obtained when the temperature of the plate is high, the drop in fact executes a vertical oscillation with a frequency which may be a few hundreds per second. If the frequency of vertical oscillation of the drop be approximately twice that of a possible horizontal oscillation, the drop commences oscillating in a star-form, in other cases its surface is merely thrown into ripples. It is shown, that for a given size of the drop, the fourth power of the width of the gap is proportional to the difference of temperature between the plate and the drop. A quantitative explanation of this result is given as due to the viscous flow of the steam outwards through the edge of the gap under the excess pressure which sustains the weight of the drop.

The experiments described above, were performed at the Laboratory of the Indian Association for the Cultivation of Science, and the author begs to record his deep thanks to Prof. C. V. Raman for his interest and help during the progress of the work.

Plate II



MERSENNE

VI. Mersenne and his Ideas on Sound

By

J. W. GILTAY, DELFT, HOLLAND

[*Translated from the Dutch Periodical*
"de Natuur" 1918.]¹

(Plate II.)

In this paper I wish to write something of Mersenne's opinions, 300 years ago, on sound in general and on the motion of strings.

Marin Mersenne was born in 1588 in La Soultière near Oizé. His father was a common farmer. Mersenne studied first in Mans with the "Pères de l'Oratoire" and afterwards in the College of Jesuits "de la Flèche," into which College Descartes at the age of thirteen also entered. In 1611 Mersenne was admitted into the order of Franciscans, in 1614 he was ordered to lecture on philosophy in the cloister of St François de Paule, at Nevers.

In 1621 he returned to Paris, where he remained, except during two voyages, one to Italy and one to Holland, in which latter country he paid a visit to his friend Descartes. He died in 1648.

Although not to the very greatest, Mersenne still belonged to the men of significance of his time. He was befriended and corresponded with the greatest spirits who studied physical and musical subjects. So, for instance, with Constantijn Huygens, with whom he corresponded

¹ Published by A. Oosthoek, Utrecht, Holland

on a controversy between Boeset and Bannius, who both had written music to the same poem ¹

Huygens called Mersenne "profond philosophe musicien, tesmoings de grands volumes qu'il en a escrit"

Mersenne has also corresponded with Christiaan Huygens on several questions of mechanics and geometry, and also on the connection between the pitch of a string and its tension ²

Poggendorff ³ says of him "dass er kein Physiker ersten Ranges war Sein Haupt verdienst mochte wohl in einer brieflichen Thatigkeit bestehen, wodurch er den Mangel eines physikalischen Journals damaliger Zeit ersetzte and viel Gutes stiftete, mitunter auch Unheil anrichtete."

Descartes, Gassendi and Thomas Hobbes often visited Mersenne, "une espèce de l'Académie s'était formée chez lui."⁴

Mersenne had a great influence on Descartes; this caused the latter totally to change the irregular life he led as a young officer.⁵

Mersenne also brought about a reconciliation between Descartes and Fermat.

If some of Mersenne's ideas strike us as rather singular, we should not forget that natural philosophers, who at that time studied acoustics, had very little ground to stand

¹ Jonckbloet and Land, Correspondence and Oeuvres Musicales de Constantijn Huygens Leide, E J Brill, 1882, p 40

² "Oeuvres Complètes de Christiaan Huygens" Publiées par la Société Hollandaise des Sciences, T I, p 30

³ Poggendorff, Geschichte der Physik, p 327.

⁴ Jonckbloet and Land, l. c, p 231

⁵ "Il s'adonna à toutes les dissipations qui sont le noviciat d'un officier de qualité Le jeune religieux blâma les moeurs de son ami, et celui ci ne s'offensa pas de ce blâme il fit mieux, il changea de conduite On s'accorde à dire que les bons conseils de Mersenne éclairèrent alors Descartes sur la vocation de son lieureux génie." (Nouvelle Bibliothèque Générale, 1861, T 25)

on Laws and rules, that we are so much accustomed to as to consider self-evident, were for the greater part unknown: the learned were obliged to find them themselves, mechanical contrivances were very few. Thus experimenting was nearly impossible, the savants spent most of their time on speculative philosophy.

We should also consider that it was then very difficult to get free of the old ideas about chemistry, alchemy and also astrology. So, for instance, the old ideas about the constitution of metals still played an important role, as we shall see where Mersenne treats on the influence of the material on the string's motion.

Only very great men were then able to achieve something of significance—mediocrities, who in our time are often able to perform some useful scientific work, were then not able to make themselves heard.

For the enumeration of Mersenne's manifold works, and also for further particulars about his life, I refer to the already named dictionary. The works I have used are "*Harmonie Universelle*," printed in 1627, and "*Traitez des Consonances, des Dissonances, des Genres, des Modes and de la Composition*," published in 1635. Of the first named book Mersenne sent a presentation copy to Christiaan Huygens.¹ Both books are rather rare. When quoting from them, I will for shortness' sake indicate them by H U and T. C.

Jonckbloet and Land viewed Mersenne chiefly from a musical point, as the correspondence with Constantijn Huygens treated only on this department. They write, among the rest, "*Il est parfaitement inutile d'analyser ces productions fort prolixes, pleines de déductions géométriques, entremêlées de digressions théologiques, etc.*"

¹ Emil Nauman, "*Geïllustreerde geschiedenis der muziek*," bewerkt door J. C. Boers, T. I., p. 543.

We shall in this paper consider only those parts of the above named books of Mersenne as have influenced the development of the theory of sound. The expression "productions fort prolixes" is very just ; but still it is, I think, well worth our while carefully to study Mersenne's works, though I cannot deny that it requires much patience to sift the physical parts from the mixture of theology, philosophy, alchemy and even astrology.

Mersenne was more a learned man than an artist. So, for instance (T. C., p. 197) he says that unisono music sounds better than many-voiced music, although it is difficult, he adds, to convince composers of this truth. He tries to prove the justice of this opinion by some very singular examples—I am sorry I cannot give them here, as they should require too much space.

To make it more evident that Mersenne was more scientist than artist, I will give some of his opinions untranslated. If the two books I have used were not so difficult to get, I should only have referred to them, but being as it is, I thought it better to copy these passages

(T. C , p. 88) " Puis que l'on connoist la proportion qui rend les sons agréables ou déplaisans, et qu'il y a de l'apparence que les autres sens requièrent de semblables proportions dans leurs objects, les sons peuvent apporter plus de lumiere à la philosophie que nulle autre qualité ; c'est pourquoy la Science de la Musique ne doit pas estre negligee, quoy que les chants ou les concerts fussent entierement abolis et defendus ; car ils ne sont pas la principale fin de la Musique, cōme croyent les Praticiens, qui mesprisent, ou ignorent la raison. En effet, si la cōnoissance des sons et de leur proportions nous peut dnonner l'entree aux proportions des objets de l'beil, de l'odorat et du goust, il n'y a point d'honneste homme qui

ne prefere cette connoissance á tous les chants, et á tous les' cécerts qui peuvent estre faits suivát les regles de l'art "

(H. U., p. 144.) " Il y a de l'apparence que ceux qui prennent plaisir á eslever leur esprit a Dieu, et qui desirent de luy offrir autant de mouvemens de leur amour et d'actes d'adoration, comme less chordes des instrumens qu'ils oyent, font de retours, ne diront pas que la cognoissance du nombre des battemens d'air soit inutile, et que ceux qui aurent assez de jugement pour considerer que la Musique n'est autre chose que le nombre de differens battemens de l'air, et que le son, à proprement parler, n'est rien, si l'oreille ne luy donne la nature du son, et quil setoit plus véritable de dire que nous sentons des mouvemens d'air, que de dire que nous osons des sons, aduouront franchement qu'il n'est pas possible d'avoir une parfaite cognoissance de la Musique, et mesme que l'on ne peut cognoistre ses principes, si l'on ne scait ce que nous avons dit des retours & des battemens."

(T C., p. 105.) " Il s'ensuit semblablement qu'un Arithméticien peut apprendere le Musique sans maistre, & qu'il n'y a nulle science si aisee, puis que ses meilleurs raisons consistent seulement a conter 1, 2, 3, 4, 6, 7 etc , & à comparences nombres les uns aux autres. Il faut neanmoins remarquer que je parle ici de la vraie Theorie, & non de la Pratique, à la quelle il faut plus de temps, dautant que le corps est plus lourd que l'esprit & qu'il faut quasi prendre autant de peine à le rendre prompt, & habile a suivre les mouvemens de l'esprit, comme pour apprendre pour les oiseaux à parler, & les autres animaux à imiter les actions de l'homme."

On p. 201 of the same book he says : " si le plaisir de la Musique consiste à en comprendre les accords, à les distinguer les uns des autres, & à considerer leur suite, il semble que les Duos doiuent estre plus agreables que les

Trios " Just as one had rather see a picture that clearly shows ("avec moins de confusion") what it means to represent.

As we see, the man of intellect is speaking here, not the artist Many-voiced music seems to have been too difficult for Mersenne to enjoy

In the Chapter on "l'Unisson" (T C, pp. 5-35), he says that the angels in heaven probably sing unisono, because that belongs more to the Trinity.

Sometimes the homeliness or simplicity of Mersenne's writings is very striking So, for instance, where he prints (H. U, p 90) several pieces of music, of which some signs or characters are wanting, as the printer did not have the types. Mersenne added these wanting signs in his own copy by means of the pen, and says that he will lend that copy with much pleasure to the possessors of his book, so that they may inscribe the wanting characters It makes a singular impression to receive this kind invitation 300 years afterwards! He adds the advice to moisten the paper first with a solution of alum, as otherwise it should blot.

As to the ideas of Mersenne about sound, it is evident that he was not quite convinced of the necessity of a motion, to produce sound, to be a vibrating one, or at least not to be of constant velocity and constant direction. So, for instance where he speaks of the motion of a bowed string (H. U, p 196), he says there that it is not necessary for a string to vibrate in order to produce a sound · if some object is pressed or rubbed against a stone, a glass disc or a piece of wood, a sound often will appear that has much resemblance to that given by a violin string, and still no vibrations are observed ("encore que l'on n'appercoive point de tremblemens ou de retours dans la friction des dits corps").

In T. C., p. 57, a similar assumption is given. There he tells us that it should be possible to hear the growing of plants, if that did not happen so slowly. On p. 135 of the same book he mentions which sound should be given by two falling stones, in the time during which they fall with velocities of the proportions of 10, 8, 6, 4 (the time to be taken so short that the velocity may be considered to be constant). He supposes the sound to get sharper if the velocity is greater "*que less buillons de l'air sont dautant plus fréquens que les mobiles se meuvent plus vite.*"

We will now first consider what Mersenne says of the pitch of strings and of the intervals

Already Ptolomeus, he says (H. U., p. 14) tells us that a cord from which a weight is suspended, is not fit to give an accurate notion about the value of intervals, as it is impossible to have a cord the thickness of which is everywhere the same, and also because its lengthening varies with the weight. Neither are flutes fit for this purpose, as the pitch of the tone they give varies with the force of blowing

Specially fit for these researches is the Monochord, of which he gives a detailed description and (H. U., p. 33) a drawing of one with three strings.

INFLUENCE OF THE LENGTH OF A STRING

Page 18, H. U., Mersenne tells us that, when a string is divided into two equal parts, each piece gives a tone an octave higher than that of the whole string. If of two strings AB and CD, the length of AB is double that of CD, so that CD gives the higher octave, then CD makes twice as many vibrations in a given time as AB. He expresses this as follows: "*la chorde AB ne battera qu'une fois l'air & ne fera qu'un tour, pendant que la chorde CD en fera deux.*"

That he knew that CD gave the octave of AB is obvious, as his sense of hearing told him that. But how did he know that the number of vibrations of CD in a given time was twice that of AB? ¹

We can show this easily by our registering apparatus, but those were unknown at that time. Mersenne has given an experimental proof of this law, as follows he stretched a string, such as is used for a spinet or a lute, of a length of 100 or 120 feet, and saw that it made one whole vibration per second. Then he shortened it to half of its former value and observed it to make two vibrations per second. If shortened to $\frac{1}{4}$, it gave 4. As it was known to him that a string shortened to $\frac{1}{2}$ gave the upper octave, he concluded from this experiment that the string giving the higher octave made double the number of vibrations.

It is rather singular that Mersenne did not give the description of this *proof* of the law (that was given on p. 16) before p. 150 (H U)

ORCHESTRA TONE.

P. 134, II U Mersenne mentions "le ton de Chapelle," what we call the Orchestra tone, and says it makes 60 vibrations per second. This nearly corresponds with B, about three octaves lower than our orchestra-a. How he did find this number of vibrations is not mentioned; he uses it to determine the number of vibrations of a string that is so short that its tone cannot be heard. I suppose he found the number 60 by the aid of a string of 120 feet, making one vibration per second, which could be verified by the eye

¹ According to Poggendorff, *l.c.*, p. 268, it was known already to Galilei that the period of vibration of a string was proportional to its length. Poggendorff says of this "Dieses Ergebnis verdient deswegen besondere Anerkennung weil mit ihm die physikalische Erforschung der Töne anhebt." As he tells us however, p. 801, that this law was also known to Aristoteles, it should be said that "die physikalische Erforschung der Töne" began with Aristoteles, not with Galilei.

just as told before, and that he found it necessary to shorten this string to $\frac{1}{6}$ of its length to get the tone B. From this experiment he might conclude that B belonged to 60 vibrations per second

INFLUENCE OF STRESS

As to the influence of stress, Mersenne mentions the following (H. U., p. 43). If two strings are taken of the same material and of the same diameter, and one is twice as long as the other, then the longer string requires a weight 4 times that wanted by the shorter to give the same pitch. With two strings of equal length and of the same material, one of which has double the thickness of the other, the thicker one requires twice as much weight for giving the same pitch as the thinner one.

This is an error of Mersenne the thicker string requires 4 times more weight than the thinner one¹

That long and short strings get the same stress by the same weight is proved by Mersenne by the fact that they both require the same weight to get broken.

INFLUENCE OF THE MATERIAL.

Of the influence of the material, Mersenne rightly says (H. U., pp. 151 and 154) that strings of heavier metal give a lower tone. Those metals containing the greatest quantity of quicksilver, he says, are heavier, those containing the greatest quantity of sulphur are lighter. Then he tries to prove that gold, "*estant le plus parfait des metaux,*" contains more quicksilver than the other metals. An exception, he says, is shown by lead. this is the heaviest, and gives a lower tone than any other metal,

¹ $n = \frac{1}{2l} \sqrt{\frac{\tau}{\pi d}}$ where n is the number of vibrations per second, l the radius, l the length, τ the stress and d the density of the material

“ encore qu'il soit plus imparfait qu'eux quant a sa solidité métallique.” We will not follow farther this long exposition ; Mersenne's ideas on this subject were the same as those of the Arabian savant, Giafar or Geber (born 702, died 765) on the composition of metals.¹

The speculations of Mersenne following on his ideas on the composition of metals, are so very curious that I cannot resist the temptation of quoting them in full : (II U , p. 156), “ Si les alchymistes nous pouvoient donner la cognoissance certaine du temperament de chaque corps par leur trois principes · par exemple quel principe pre-domine en l'homme, qui a 4 degrez de cholere, de ioye ou de tristesse ; & supposé qu'un homme pese cent livres, combien il a de livres de chaque espece de sel, combien de souphre & de mercure tant en poids qu'en grandeur , quel principe se diminue, s'altere ou s'augmente en toutes sortes de maladies & de passions de l'ame , combien chaque repas augmente les trois principes, combien il s'endissipe tous les jours , en quel poids & en quelle quantité les trois principes se doivent rencontrer en celui qui a les qualitez d'un musicien, & en quelle quantité & en quel poids ils sont en chaque metal, ils nous soulageroient gradement, & nous obligeroient a suivre la maniere de raisonner tant en ce qui appartient aux sons, aux pesanteurs, qu'aux autres qualitez des corps, dont j'ai traité desjà dans le livre de la Theorie selon leur principes. Mais si l'on veut donner la raison de la diversité des sons sans sortir de la Philosophie, ou de la Medecine ordinaire, il faut dire que le son le plus grave vient du metal, ou du corps le plus terrestre & le plus pesant, et qui a plus d'eau meslée avec sa terre : car l'on experimente que plus un homme a de bile de cholere, & plus il parle haut & aigu ; ce que est représenté par les cordes des instruments

¹ Poggendorff, I c , p. 60.

qui sont les plus déliées & les plus courtes, & par toutes sortes de mouuements qui sont brusques & legers ”

INFLUENCE OF GRAVITY.

(H. U., p 43) If a stretched string is placed in a horizontal position, it is bent by the law of gravity, just like a cable drawing a vessel. Mersenne concludes from this that stringed instruments should have “un autre effect” when placed horizontally than when placed vertically.

INFLUENCE OF HUMIDITY.

When a stretched string is moistened, it shrinks, the tension thereby getting larger and the pitch higher. Mersenne proposes to use this for the construction of a hygroscope; the moistness of the air to be measured by the change of pitch, or by the variation in length of the string.¹

He also mentions the well known application of this property of a string or a rope, made by Fontane for raising an obelisk before St Peter's Church at Rome. The rope was somewhat too short; by being moistened it shrank sufficiently for placing the obelisk in a vertical position.² The explanation given by Mersenne of this shrinking is most singular.

DURATION OF THE VIBRATION.

(H. U., p 45.) How long a plucked string will continue to vibrate is very difficult to say. A string or cord, suspended at one end and provided with a weight at the other

¹ Such a hygroscope has been described already by Leonardo da Vinci (1452-1519) (*Libri, Histoire des Sciences Mathématiques en Italie*, Halle & Saale, H. W. Schmidt, 1865, p 53)

² I remember, some 50 years ago, the transmission of lathes, driven by the foot, was often made by a rope instead of a leather belt. If the rope got too slack, it was shortened by moisture.

end, will swing during half an hour. The vibration of a string, fastened at both ends, soon gets too small to be visible. Strings of 3 or 4 feet vibrate, visibly to the eye, about 10 times per second (10 beats of "un poux bien regle") This vibration is visible because the middle of the vibrating string seems to be thicker than the ends. Mersenne supposes a string 3 or 4 feet to vibrate during 20 seconds; if it makes 100 vibrations per second, it makes 2,000 before stopping. He supposes a long and a short string both to make the same number of vibrations before stopping.

In this unfertile reasoning Mersenne forgets that the largeness of the first elongation has a great influence on the duration of the motion

MINIMAL VELOCITY OF MOTION

(H U, p 140.) Mersenne has also determined with what velocity a string ought to move in order to make a perceptible sound. He supposes a plucked string to begin with an elongation of $\frac{1}{11}$ of a line, and that the ratio of two following elongations is as 12 : 11. He has calculated the elongation of the 132nd vibration to be $\frac{1}{100000}$ of the first, and as a plucked string can be heard over a period of 2 or 3 seconds, he concludes that the velocity of the string is then less than one "pouce" per second, or less than 5 feet per minute. He adds that this velocity suffices to take a walk of 60 paces, if one walks slowly, and that it corresponds with the velocity with which a tortoise moves.

The exactness of these numbers—the worth of which, even when they were exact, should be of little consequence—is very dubious. The period of vibration is not given. It might be determined perhaps from the fact that the 132nd vibration takes place after 2 or 3 seconds; at least that is what I suppose Mersenne to mean.

LOWER LIMIT OF PERCEPTIBILITY.

(H. U., p 138.) Mersenne gives some very queer remarks on the lowest number of vibrations it is possible to hear as a continuous sound.

Firstly he describes the case of a string plucked 30 times per second. As a string, making 30 vibrations per second, gives a continuous sound, he concludes that a string, plucked 30 times per second, will also produce a continuous sound so that a tone of 30 vibrations will be heard and not the separate shocks. The same happens, he says, when a string is *bowed* 30 times a second. If the bow itself also produces a tone (by the vibrations communicated to it by the surrounding air) then this tone will have the same pitch as that of the string. But it would be much feebler than that of the string, because the bow "*toucherait moins d'air*" If the string is drawn (plucked) from its position of rest 10 times per second, then we have to do with another case. One then hears only the separate shocks, instead of a continuous sound. Only when the shocks are all of the same intensity, so that every shock produces the same sound, he says, one will hear, even with this small number of shocks, a continuous sound. If the elongation diminishes, the ear will perceive the shocks separately ("*comme si ils faisoient des sons differents*"). But the ear, he adds, is probably not sufficiently sensitive to perceive such small differences.

These pages (138 and 139) are far from clear, obviously the subject was not clear to Mersenne himself. With "*des sons differents*" he probably means tones of different pitch.

Of the *pitch* of the strings with which he experimented, nothing is said. Perhaps they were tuned respectively to 30 and 10 vibrations per second.

As is well known, a sound produced by 10 shocks a second is not continuous ; whether the shocks are all of the same strength or not is indifferent, as can be proved by Savart's toothed wheel.

NUMBER OF TONES GIVEN BY A STRING.

(H. U , p. 42.) In order to learn how many different tones a string can give, Mersenne determines the weight necessary to break it, in other words, he determines the stress it is able to bear.

RATIO OF DAMPING.

(H U., p. 43.) According to Mersenne, the ratio of the elongation of the $n - 1^{\text{th}}$ vibration to that of the n^{th} is constant, the diminution being according to a geometrical series. We have already seen the application of this rule, where he treated on the minimal velocity. He gives a list of the amplitudes of a plucked string, for the damping he gives $\frac{1}{11}$, as before. If the first elongation or amplitude is 10^{60} , then the 1584^{th} is $= 1$, as he has calculated. This 10^{60} is given in full $\cdot 1$ with 60 zeroes behind it, the other numbers are printed in the same wise. He gives those values for 35 different elongations.

With all respect for the knowledge and the working power of Mersenne, we can only wonder at his having spent so much time at this useless work.¹

CONSONANTS

(T. C., p. 88.) Although we do not know, he says, why consonants are agreeable to our hearing, we know the proportion that must exist between two tones to form a

¹ Such kind of work is called in Dutch "monnikenwerk" (monks' work). One gets the same impression from what Mersenne says of the total number of vibrations, given by 44 instruments, during the time that they played 22 measures of an aria of Böeset. (H. U , p. 140).

consonant. We learn therefrom that we know more of sound than of colours and of taste. "Car on ne connoist nullement combien une couleur doit avoir de degrez de lumiere, ny combien une odeur doit avoir de degrez de chaleur pour agreer, & l'on n'est pas encore demeuré d'accord de la couleur, de la saveur, ou de l'odeur le plus agreable," while everybody will find the octave and the fifth agreeable to the ear: "ce qui monstre que les sons aprochent plus près de l'esprit & de l'intellectuel que l'objet des autres sens"

MOTION OF A BOWED STRING.

(H. U., p 145.) Mersenne has given much thought to the motion of a bowed string. He says the following about this if it were possible to pluck a string, tuned to 64 vibrations, 64 times per second, or to put it into motion by 64 strokes of the bow in that time, it should be impossible to count the motion of the finger, the bow and the string, as one cannot follow by eyesight more than 10 vibrations per second. But it is difficult to understand how such a string can give a tone if the bow makes 64 strokes per second, for if the number of vibrations is not larger than that of the strokes, it seems to follow from this that "le mouuement de l'archet soit une mesme chose avec les dits tremblemens - en suite de quoy il faut dire que la chorde aurait le mesme son, quoy qu' elle ne tremblast point, d'autant que celuy qui la touche, supplée le tremblement que vient de la tension, de la chorde, puisqu'il luy fait faire 64 tours & autant de retours dans l'espace d'une mesure; mais je traiteray de cette difficulté dans le discours de la Lyre."

I may add to this that I did not find anything about the motion of strings in that part of the work that treats on the "Lyre."

H. U , p 196, Mersenne returns to this subject: If two strings give the same tone, they undoubtedly make the same number of vibrations in a given time, as the string necessarily makes the same number of vibrations, whether plucked or bowed. But he was not quite sure of this. As the bow, he says, pushes (or draws) the string in the same direction during one stroke, it will seem to be that the string cannot move *against* the motion of the bow, as it is kept fast by the bow. ("il semble qu'elle ne peut reuenir a contresens & au contraire de l'archet, qui la tient en mesme estat, & qui la conserve dans la situation qu'il luy a donnée, lorsqu'il l'a poussée iusques où elle a peu aller.")

As the reader will perceive, just that what Mersenne considered to be impossible really happens, as Helmholtz showed 250 years later by his vibration-microscope. But, he continues, it is not necessary for a string to vibrate in order to produce a tone, he then again describes the experiments with rubbed stones, etc , as told before.

Still it is not to be supposed, he continues, that the string under the bow makes as many vibrations as under the finger ("dessouz le doigt"), by which he probably means, when it is plucked. The string should produce no sound at all, or also quite another sound, if the bow pushed the string from right to left (or the reverse) in such a manner that it could not vibrate freely. ("auoir leurs retours libres"), unless the object that pushes the string (the bow) makes itself as many vibrations as the string ought to make, just as happens when the wind blows against a rock or a tree.

As the sound of a plucked string is somewhat different from that of a bowed one, although the pitch is the same, Mersenne concludes that the bow ' y contribue quelque chose, ce qu'il fait en froissant la chorde & en renfermant de l'air entre elle et luy," which air is then forced

to make as many vibrations as the string. Further he says that the bow hinders the string's vibrations which is the cause of their being not so large as is the case with a plucked string. He evidently means that the motion of the string is stopped every moment by the bow and tries to explain this by the example of a flute a hole of which is stopped in rapid succession. In that case the character of the sound is altered, but the pitch remains the same, just as in the vibrating tones often heard from a singer. And as the hairs of the bow do not form a continuous body, the air, put into motion by the strings, will easily enter the space between the hairs, the motion and the pressure of which may alter the sound. When one keeps in mind that the vibrations of the atoms of the air or of the string mix with the vibrations of the bow's hairs, one cannot wonder that the sound, produced by those two motions, is different from that given by the string alone.

That the number of vibrations of a string in a given time is the same, whether bowed or plucked, has been proved by Mersenne with a cord of 100 feet, in both cases it made one vibration per second.

That the bowed string really vibrates, he continues, can be felt by touching it with a finger. That the pitch remains the same, whether the motion of the bow is slow or fast, proves that the sound is produced by the string and not by the bow.

I have treated this chapter on the motion of the bowed string so elaborately, as it seemed to me to be of much interest. As the reader will have perceived, Mersenne has sought to understand it by several ways, that he did not succeed however to solve this difficult problem, we cannot wonder at, as the necessary instruments of research did not exist at that time, and especially as the great influence of the *form of vibration* was not then known.

TONE COLOUR

We will now consider what Mersenne tells about the difference of sounds of the same pitch, what we call tone colour or timbre

The difference of timbre of a bowed and a plucked string has been treated in the foregoing section, as also the explanation Mersenne tried to give of that phenomenon

The question which instrument gives the most agreeable sound cannot be answered (H U, p 10) The violinist will find his instrument the best, the hornblower will speak for his horn, the soldier prefers the trumpet, the hunter his buglehorn, etc The sound given by a beaten string ("une corde frappée") is divided by Mersenne into two parts (1) that which arises at the moment of striking, (2) that caused by the vibration after this moment The first named sound has some resemblance to that of an organ pipe with vibrating tongue, it is sharp and somewhat rough¹ The second sound is much mellow and resembles that of a flute ("Flute d' Allemand"), it is called by Mersenne "le second son" or "le son de resonance"

The duration of the first sound is very short; that of the second is larger, but this sound is steadily getting feebler, till it is no more perceived An instrument able to give a "son de resonance, et qui participait en quelque sorte de la percussion" should be perfect Some notion of this sound is given by the lute when the wind causes the strings to vibrate (Æolus' harp)

When a violin is played skilfully, the first sound ("le son de percussion") is mellow than that of a beaten string, and the duration of the first as well as that of the

¹ One should keep in mind that the strings of the spinet (the forerunner of our pianoforte) were beaten by steel pens or by goose quills, and not, as now is the case, by hammers covered with felt

second sound has the same value as the duration of the bow's stroke. So that we have two sounds at the same time, one gay or cheerful and agreeable, the other mellow and "harmonique." Mersenne concludes from this that the violin comes nearest to a perfect instrument. But, he continues, the first sound of the violin always is somewhat crude, so that it is better to hear a violin from some distance. The most beautiful sound one can conceive would be that of a lute, when the first sound could be eliminated—that should equal that of a violin able to sound without the use of the bow (*resonante sans archet*). That kind of music should be perfect, "*mais elle est réservée pour les bien-heureux au Ciel ou elle sera dénuée de toute l'imperfection qui s'y retrouve maintenant*."

Although rather quaintly expressed, there is some truth in this reasoning about the sound of the violin. The string is, at every moment, carried away by the bow, and there is some resemblance between this motion and that of a string being beaten.

The mellowness of sound, Mersenne says, depends upon the choice of the string, and also upon the manner in which it is put into vibration. Strings of gut give a mellower sound than those of metal. From two strings of the same material and unequal length, tuned to the same pitch, the longer will give "*un son plus doux*" and the shorter "*un son plus plein et plus massif*." The manner in which a string is plucked by the finger has also great influence on the tone colour. The sound is mellower when the string is plucked by the finger than when plucked by a metallic pen or an ivory plate. That is the reason for the sound of the harp and the lute being mellower than that of the spinet.¹

¹ Cf. the foot note, p. 90

The sound of the violin alters with the spot where the string is bowed or plucked. If this is far from the bridge, the sound is mellow, if near to it, it is sharper. Mersenne of course was not able to explain this, as he did not know anything about the leaving out of overtones (harmonics), and the influence on timbre caused by it. As the reader will have perceived, Mersenne's observations were quite correct however.

THE VIOLIN

We have already mentioned Mersenne's ideas about the sound of the violin. Of the significance of the different parts of the violin he does not say anything, he only mentions (H. U., p. 193) that he will afterwards explain why the soundpost should be placed under the right foot of the bridge, and also why the sound of the violin is not good, when the soundpost is not placed on the right spot, or when it is removed altogether. I have not been able to find those two explanations in the two books I have used, however.

Of all instruments, he says, the violin is the most fit to imitate the human voice, *i e.*, the human song.¹ One stroke of the bow takes about as much time as the period of one respiration. The violin is also "le plus propre de tous pour faire danser" (H. U., p. 177.)

Pp. 181 and 182, H. U., have been devoted to teaching one to play the violin. "Expliquer la manière de jouer du violon & de mettre chaque doigt sur les endroits de la touche pour jouer toutes sortes de pieces de Musique."²

¹ One of my friends played the violin, a boy of some 3 years old heard it and when the piece was finished, he said "Please, Sir, do sing something more."

² One would be apt to think from this that one can play the violin, if only the fingers were put on the right spot of the string. It reminds me of the prudent answer, given by a Scotaman, when asked whether he could play the violin "He did not know for sure, he had never tried it."

OVERTONES (HARMONICS)

H. U., p 55 The strings of the lute give also other tones than those generally heard (*i.e.*, other than the fundamental notes); these are called "naturals." If for instance a string of 1 foot length is plucked in a spot one foot from the end, one hears a "faux son," belonging to a length of string from the finger to the nearer end of the string, and one hears also a tone belonging to a string of 3 feet. The first tone is called by Mersenne "le Quintiesme" (we should call it the double octave), the other the fifth of the fundamental. The finger in this case replaces the bridge, he adds.

This is not exact A string, plucked at $\frac{1}{4}$ of its length, does not give even overtones, as it gets a ventral spot just there where even overtones should require a node Evidently it is impossible that the double octave should appear in this experiment; no more can the fifth be expected, as this *never* is an overtone of strings. Obviously Mersenne has confounded this experiment with that of a sonometer string having a bridge at $\frac{1}{4}$ of its length, in which case the pieces of string *whether*

It should be considered however that at the time of Mersenne violin playing was much easier than it now is Harmonics were not played and it was very seldom that higher positions were used, as the violin mostly was used for accompanying the soprano voice and thus went no higher

Stoeving, treating on harmonics, says of Domenico Ferrari (died 1780) "To him is ascribed, if not the invention, at least the first more extensive use of harmonics on the violin" (Paul Stoeving, *The Story of the Violin*, the Walter Scott Pub Co, London, 1904, p 183) Playing harmonics came to its own and perhaps more than that by Paganini According to T L Schubert ("*die Violine*," 4th Ed, 1892, p 19) the second position was not used before 1800 Stoeving however says that in a "*Capriccio Stravagante*" of Carlo Farina, about 1726, the second position was twice used. This was then considered to be so very difficult that the composer was obliged carefully to instruct the player how to make those notes If c" was played on the violoncello, connoisseurs among the public often made their neighbours attentive on this hazardous enterprise (Heron Allen, "*Violin-making as it was and is*," Ward, Lock & Co, Ltd, London, p 58) Mersenne mentions the possibility of playing d" on the e-string of the violin

plucked or bowed, show the double octave and the fifth. That he confounded those two experiments is also made evident by his saying that the finger (in the first named experiment) replaces the bridge.

Generally one does not hear those overtones, Mersenne says, as the fundamental covers and extinguishes them. But if the vibrating string is touched by the nail of a finger, they are more easily heard; the tone belonging to the longer end of the string is always heard best. *Which* overtones are heard in this way is not said, nor *where* the string is to be touched.

The overtones are not caused (H. U., p. 195) by the number of guts ("le nombre des intestins") of which the string is composed, as metal strings show the same overtones. The lower strings of the lute and the violin are the best for experimenting on overtones, they give the octave, the major third of the octave ("le Dixiesme maieure") and the fifth of the octave ("le Douziesme du premier son"). This is rather inaccurate. the major third named here, is taxed an octave too low, it is the major third of the *second* octave (the fourth overtone, *e'* when C is the fundamental).

According to Mersenne, Aristoteles was already acquainted with the existence of overtones, but he did not know that a plucked or a bowed string was able to give at least 5 different tones.¹ Mersenne speaks only of the tones of the free strings ("chorde touchée à vuide"), it seems he has never made these experiments with stopped (shortened) strings.

As to the number of vibrations, he justly observes that they are always in the proportion 1, 2, 3, 4, 5....

Of the overtones of organ pipes he has observed only the 12th tone, *i.e.*, the second overtone. He very justly

¹ Helmholtz observed 16 overtones when experimenting with thin strings

gives the reason why the 12th and the 17th (the second and fourth overtones) are more easily heard than the first and the third

It is unexplicable, he says (H U , p 155) how a string can beat the air ("battre l'air) 5, 4, 3, 2, times in the same time in which it only does *once*, unless one supposes that the half of the string makes two vibrations in the same time the whole string makes one, and that also the 3rd, 4th and 5th part make 3, 4, 5, times more vibrations in a given time than the whole string does

As the reader will perceive, Mersenne in this paragraph very nearly gives the true explanation, but yet rejected it the experiment, he says, shows clearly that all parts of the string have the same velocity (read —have the same period), for the string has but one motion, although the parts nearest to the bridge and the saddle move more slowly than the middle part of the string.

The lowest tone (the fundamental) is not given by the ends of the string, as they move more slowly than the middle. The lowest tone is the strongest of all six, it follows therefore that it is caused by the middle of the string, as that makes far greater elongations than the ends do.

Mersenne tries to explain the existence of overtones (H U , p. 210) by reflection of the air against the string and by a splitting of the air particles "l'on peut dire que les diferentes parties de la chorde qui frappent l'air differemment, diusent & rompent la sphere de l'air en 2, 3, 4, 5 parties, ou que la mesme partie de la chorde le rompt differemment selon les diferentes dispositions, de sorte que l'une des parties de l'air se rompt en deux, l'autre en trois, quatre ou cinque parties, etc."

I will not say more of this singular speculation, as it is very difficult to render and too long wholly to quote it. As to the assumption of some scientists that a string

is to be considered as a set of coaxial cylinders ("comme les peaux d'oignon se couvrent les unes les autres") and that the inner cylinders produce another tone than the outer ones, Mersenne does not believe that.

P. 395, H. U, he again speaks of the overtones of stopped pipes. He has observed them to give the fifth of the octave (the second overtone). Not all pipes do that, he says, even when they are exactly of the same dimensions. Whether they that do give this tone are better or worse than those that do not, he does not know. The lower tone (the fundamental) is always the stronger of the two

But it is difficult, he says, to understand how it is possible for the air to make one and three vibrations at the same time. It is possible that the three vibrations do not take place at the same time with the one vibration, but so soon afterwards that the ear does not observe the interval of time. But this explanation does not satisfy him either, for why should the air prefer to make three vibrations instead of four or another number? He supposes the octave is also produced, because "trois suit plus naturellement & plus immédiatement deux, qu'un". But he thinks it is not heard so easily, because of its great resemblance with the fundamental

According to some, he says, the fifth of the octave is sometimes heard also out of the singing in the church, he has never heard it himself however. Whether this happens by a kind of echo, or whether "l'artere vocale" acts as an organ pipe he does not know.

"Or, cette experience estant supposée, ie dis qu'il se fait de petits retours d'air dans chaque grand retour du mesme air, avec lequel ils ont mesme raison que les deux sons de la Douziesme ou de la Quinte, & par consequent que chaque partie d'air, dont le mouvement dure un moment en faisant le son grave, endure encore en soy

quelque sort de tremblement ou de fremissement semblable a celuy des cloches tremblantes, ou de l'eau qui fremist dans une verre, lors qu'on le fait sonner en passant le doigt sur son bord, & que l'air est trois fois agité parces petites secousses, tandis qu'il fait chacun de ses plus grands retours."

The same can be said, he continues, of the tones of a string, for each small vibration can be divided into smaller ones. If the hand is moved to and fro, and if it makes at the same time also smaller motions, one gets a motion of the vibration of the air in an organ pipe.

As the reader will have perceived, Mersenne actually speaks here of the *form* of a motion.

It would be possible, he says, to speak with more knowledge on this subject, if we were able to see and count the vibrations of the octave and the duodecime, just as we can do that for the fundamental. He does not think this to be impossible, as small vibrations can be seen by a "lunette convexo-concave."

As we see, Mersenne has tried to explain the existence of overtones in all possible ways, just as he did for the motion of bowed strings. In both cases however in vain, though he has been very near to the solution of the mystery. He ends his study on overtones with so very curious a speculation, that I will quote it in full (H. U., p. 211) "Si le son de chaque chorde est d'autant plus harmonieux & agreable, qu'elle fait entendre un plus grand nombre de sons differens en mesme temps, & qu'il soit permis de comparer les actions morales aux naturelles, & de transporter la Physique aux actions humaines, l'on peut dire que chaque action est de plus harmonieuse & agreable a Dieu, qu'elle est accompagnée d'un plus grand nombre de motifs, pourveu qu'ils seroient tous bons ; par exemple lorsque l'on jeusne pour macerer

le corps, & poun le rendre plus obeyssant à l'esprit ; & puis pour satisfaire au commandement de l'Eglise ; en troisieme lieu pour reserver quelque chose pour les pauures, & finalement pour imiter les jeusnes de nostre sauueur, & pour pratiquer l'amour que nous luy portons. Car l'on peut comparer tous ces motifs à tous les sons qui accompagnent le mouuement de la chorde, & dire quant & quant que l'intention qui est la plus forte, & qui a la fin la principale & la plus excellente, est semblable au son dominant & naturel de la chorde, puis qu'il est le plus sensible, & la cause de tous les autres sons qui se font par des mouuemens odus precipitez, ou par des retours plus frequens."

HARMONICS

(H U., p 220.) In Mersenne's works very little is said about harmonics. He gives a description of the "trompette marine," a very long bowed instrument with only one string¹ When played on, the string is lightly touched with the finger (not stopped), at $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ of its length, so that only harmonics will appear. If the string is touched at a spot not located exactly at $\frac{1}{2}$, $\frac{1}{3}$ of its length, one gets sounds of which Mersenne says "on ne peut quasi juger de leur ton Quoy qu'il en soit" he continues, "il tremble si mal à ces points que leurs sons ne valent rien & qu'ils sont fort desagrables . & il suffi que j'ai expliqué les veritables Phenomenes de cet instrument pour donner occasion aux bons esprits d'en rechercher les vrayes raisons."

As the reader perceives, Mersenne does not understand why the trompette marine only gives harmonics and

¹ This is no trumpet and has nothing to do with the navy It is called so because its sound has much resemblance with that of a trumpet, a "marine," because it was invented by Marino or Marigni (Poggendorff, 10, p 811) The Dutch name is "linen," the German "Trumscheit"

leaves it to others to find the explanation. As the string of this instrument is only lightly touched, not stopped, it is evident to us that it is only able to give harmonics. As soon as the string is stopped, it is of course possible to produce other tones, as Mersenne himself remarks. It is rather strange that he has never tried this with other bowed instruments, in which case he should have found exactly the same phenomenon.

BEATS.

(H. U , p. 362) If two organ pipes, differing somewhat in pitch, are blown at the same time, they "so font trembler", this does not happen when they are tuned exactly to the same pitch. This can be felt by touching the pipes by the hand

This is what we call beats. Mersenne ascribes the phenomenon to resonance, one pipe forcing the other to co-vibrate, and wonders that a string can be brought to co-vibrate more easily by another when they are exactly at the same pitch, while the pipes, in order to produce those "tremblemens," may *not* be tuned exactly unisono. He has tried in vain to get beats from strings.¹

It is remarkable that Mersenne has been very near to having found the cause of those beats, as the following shall show. If two tones are produced at the same time, the ratio of whose numbers of vibrations is 16 . 15 or 25 . 24 or 88 : 80, each pair gives the same number of beats per second. "Puisque ces mouuemens ne conviennent & ne s'unissent point ensemble qu'au 15, 24 ou 80 coup, il semble qu'on deurait remarquer quinze ou vingtquatre battemens."

¹ This is rather singular. If the c and the g string of a viola are not tuned exactly to fifths, they give very perceptible beats together, when bowed at the same time.

While at first he sought the origin of beats in resonance, here, as seen by the expression "s'unissent," he really gives the true explanation. Obviously he did not think of the periodical changes of intensity, caused by "s'unissent."

He also mentions that an organ pipe can give beats with a string, and the probability of being able to tune the pipe to accord with the string. One can also, he says, tune the organ solely by the aid of beats.¹

RESONANCE.

(II U., p. 136) The most beautiful sound ("une harmonie rauissante") is given by a string when tuned to the pitch of the belly of the instrument. The enclosed volume of air also influences the sound.

The sound of the string (p. 145) is very difficult to hear when the air, put into vibration, is not shut up and when the motion of the air (the sound wave) is not reflected, as happens by means of the belly and the soundbox of the musical instruments.

Mersenne seems to consider resonance to be caused by reflexion only. Perhaps he thought of the echo, when treating this. The explanation given by some scientists that a string can only cause another to co-vibrate when they are unisono because of sympathy or antipathy (T C, p. 26) he rejects. As he truly says, the introduction of such words serves only "pour confeser ingenue-ment qu'ils n'en scavent rien." The same could be said, he continues, of the sympathy between magnet and iron,

¹ As is well known, this method is followed for making accurate tuning forks.

As a curiosity, I may mention here that Mersenne gives several rules and a table for enabling the deaf to tune bowed and plucked instruments.

(H U., p. 123) It reminds me of Laputa, where the blind were used to mix colours for the painters.

amber and straw, etc. As soon as the causes of these actions shall be understood, "le sympathie s'évanouit avec l'ignorance"

Mersenne shows, by means of a drawing, how of two strings of the same pitch one puts the other into co-vibration by means of the surrounding air. The difference of phase can be seen in the figure

P 52 (T C) He tries to explain how a vibrating string can cause another to co-vibrate when the difference of pitch is an octave. He refers to his explanation of the resonance of two unisono strings, and says that the only difference between the two cases is "que celles qui sont à l'octave ne se font pas trembler si fort à raison qu'elles ne se rencontrent qu'à chaque deuxiesme coup"

This might be true if the inducing string did give only *shocks*, just as in the case of a churchbell being rung, when the cord is drawn only once for two whole swings of the bell. That Mersenne really considered the vibration of strings as being made up of shocks, follows from what he says of a string making 60 vibrations per second. "elle bat l'air 60 fois par seconde minute". He sometimes compares the time taken by a string to make one vibration (un tour et retour) with the motion of the human pulse, which he takes to be 60 beats per minute.¹

Evidently he did not at all think of the *form* of the vibration, although he has been very near to have a true notion about it. It is singular that Mersenne did not find that the resonance of strings with a difference of an octave was caused by the first overtone, the existence of which was known to him. If a string 1, tuned to a" is

¹ It will seem from this that men were more calm at that time than they are now. Cardano (1501-1576) used the number of beats of the pulse for measuring the velocity of the wind (Poggendorff, 1 c, p 123)

vibrating, a string 2, tuned to a", will co-vibrate by the first overtone, a", of string 1. If 2 is bowed, it will cause 1 to divide itself into two halves, each of them giving a". That the resonance of strings with a difference of an octave is not so great as that of unisono strings is evident, as the overtones of strings are always weaker than the fundamentals. Mersenne evidently was not sufficiently impressed of the significance of overtones, although he knew them to have a physical existence.

P 67, T. C. He tells us that a bowed or a plucked string can also force another, tuned to a fifth higher, to co-vibrate. The resonance however is more marked with a string tuned to the "Douziesme." The first is not true: the duodecime co-vibrates, but the fifth does not. Mersenne has committed the mistake to take the fifth of the octave for the fifth of the fundamental.

HOW TO INDICATE KEY NOTE AND TEMPO

(H. U., p. 148.) To cause a piece of music to be played in the required key, Mersenne proposes to write beside the first note the number of vibrations per second it is intended to make. Tuning-pipes and tuning-forks did not exist at that time; instead of them strings were used whose number of vibrations was known.

By following this rule, he says, it is possible to play a piece of music exactly in the same key in Paris and in Peking.

For indicating the tempo, the use of a pendulum is advised, the time of one swing corresponding to the period of one measure. It may also be done, he says, as follows: if the first note of the piece has for instance 50 vibrations per second, and one measure is to last 2 seconds, this can be indicated by writing the number 100 beside the first note.

Why he does not indicate the duration of the measure *in seconds* is not easy to understand

A pendulum is much cheaper, he adds, than a clock, for measuring the number of beats of the pulse and for astronomical observations it should also be used ¹

THE PENDULUM

Mersenne has also written about the motion of the pendulum. Although this strictly does not belong to our subject, I shall mention something of it

He has been the first who tried to determine the length of a pendulum giving seconds, his results however were not very accurate ². It was known to him that two pendulums of equal length do swing synchronously only then when their elongations have the same value, or when they are very small. He took two pendulums of equal length, the first made elongations of 2 feet, the other of 1 inch, and observed that the first made 30 or 40 swings in the time that the second made 31 or 41 ³

The weight of the bob has no influence on the time of swing, as light and heavy objects fall with the same velocity. This cannot be explained, he says, by supposing heavy bodies to excite more resistance from the air, as an iron and a wooden ball of the same size fall with the same velocity. What should happen in an empty space, we do not know "*parce qu'on ne scait pas si le vuide est*

¹ Pendulum clocks did not then exist, they were invented in 1656 by Christiaan Huygens. Before that time clockwork with a horizontal balance was used (Poggendorff, 1 c, p. 600, Fig. 30) or such with a wind vane. Galilei intended to connect the pendulum with a set of toothed wheels, for simplifying the counting of the number of swings. As he had already lost his eyesight then, his son at his request made such an apparatus, that was described in 1649. But as these clocks were not provided with a driving weight, of course they soon came to a standstill. They were moreover unfit for measuring the time, as the elongations gradually got smaller, as also did the time between two following swings.

² Poggendorff, 1 c, p. 325

³ This had been observed already in 1583 by Galilei (Poggendorff, 1 c, p. 289)

possible, ny s'il est quelque chose de réel " Therefore we do not know whether a pendulum, to which an elongation is given in an empty space, should fall back to its vertical position or not, and if it did, with what velocity that should happen

This notion of Mersenne is in accordance with the ideas of Aristoteles about the fall, who thought that the acceleration was caused by the air following the falling object and continually giving it a new impulse¹

It is evident that Mersenne, who ascribed this singular effect of falling objects to the air, did not dare to foretell how a pendulum should behave in vacuum, as after all the pendulum is driven by the same force that causes a body to fall

AUTOMATICAL MUSICAL INSTRUMENTS

It is very remarkable that in Mersenne's works some instruments already are described that are the forerunners of our pianolas and our automatic violins. P 106, H. U., he describes a clavecymbal, invented by a German, that is able to make a sound like that of the violin. The strings are put into vibration by rotating cylinders, the surface of which is covered with leather, the cylinders being rotated by toothed wheels and springs. This is obviously the forerunner of the automatic violin, invented in America, some years ago². It is a pity that Mersenne does not give a drawing of this instrument, the more so as he himself says "ce qui est mal aysé à comprendre sans en voir la figure, dont je parleray après"³

¹ Poggenдорff, I c, p 220

² Electrical World (New York), Vol 55, p 764

³ It makes an agreeable impression in this period of international hatred to hear the following opinion of a Frenchman "les Allemands sont pour l'ordinaire plus inventifs et ingénieux dans les Mécaniques que les autres Nations, & particulièrement ils redoublent mieux à l'invention des Instruments de Musique "

The idea of causing a string to vibrate by rollers had already been applied in Mersenne's time to a kind of lyre.¹

P 214, H U., Mersenne says that it is not possible to get the same effect with these rollers that one can get by the use of the bow "l'on n'a pu suppléer les mouvements de la savante main de ceux qui charment les oreilles par les instrumens à manches touchez & non touchez" He obviously had more musical taste than the American who 300 years afterwards invented the automatic violin.

P. 160, H. U., he tells of an instrument that might already be called a pianola (mechanical piano). It is moved by springs "Et je ne doute pas que l'on ne puisse remplir une ville tout entière de musique, de sorte qu'il n'y aura nulle maison qui n'ait son harmonie, lorsqu'on lâchera quelque ressort."²

P 372, H U., he tells us of an instrument that represents at the same time an organ and a piano, as it is provided with strings as well as with pipes. If this instrument is altered in such a manner, he adds, that it is also able to give the sound of the violin, "il semble qu'il n'y aura plus rien à désirer dans l'Orgue, si ce n'est que ses tuyaux fassent entendre les voyelles et les syllabes, ce qu'il ne faut pas espérer pour la grande difficulté qui s'y rencontre."

Mankind has had to wait about 3 centuries for this desideratum, when first Faber's speaking machine and later Edison's phonograph was invented.

¹ The Dutch name is "dinkriet" or "rotteveel, a violin ("vedel," in old Dutch) being put into motion by a wheel "rad," "rotte," from "rota" The word Rotteveel still exists as a family name in our country

² Similar instruments were also made in Holland at that time Peter Pampus, instrument maker in Amsterdam, made an automatic piano ("clavecimbel") that was tried by two organists in 1628, ("Oud Holland," p 72)

We have already seen several examples of the sudden leaps made by Mersenne from physical science to philosophy or theology.¹ I will end by quoting one of the most remarkable digressions I found in Mersenne's books. (H. U., p. 146): "mais afin que l'on ne quitte pas ce discours sans en retirer quelque profit, il me semble que les musiciens doiuent considerer que puis que les chordes qu'ils touchent, ne leur refusent iamais leur mouuemens, & qu'elles obeyssent très-promptement à leur volonté iusques à se rompre, quand il leur plaist, qu'ils doivent imiter cette obeyssance si ponctuelle en suiuant la volonté de Dieu, & les bons mouuemens qu'il leur donne pour faire le bien & pour euitier le mal car puis qu'il n'y a nul mouuement qui ne conduise au premier moteur, il est tres-raisonnable que les mouuemens, dont on recoit de si grands contentemens, & d'ou on tire une si grande harmonie, nous menent à celui, dont la Prouidence bat incessamment la mesure de l'harmonie de l'Univers, & gouuerne le grand concert de tout le monde, de peur qu'il soit dit dans d'Eternité que les musiciens ont esté plus stupides & plus irraisonnables que les creatures inanimeés, & qu'ils soient si malheureux que les chordes, dont ils ont tiré tant d'harmonie, seruent au grand iour du Iugement pour les her & les affliger, s' ils ont si peu d'esprit and de iugement qu'ils ne rapportent pas l'harmonie de leurs chords, & de leurs voix à la gloire de celui qui seul merite les louanges de toutes les Creatures, que le Prophet Royal exhorte à leur deuoir par ses dernières paroles, "omnis spiritus laudet Dominum."

¹ Some of them reminded me of Silas Wegg's "falling into poetry" when reading the Roman History in Dickens' "Our Mutual Friend"

VII. Investigations on the Acoustics of the Pianoforte : I

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1. Introduction.

In a paper published in the Proceedings of the Indian Association for the Cultivation of Science, Vol. VII, parts I and II, Mr Panchanan Das has given an equation for the pressure exerted by the pianoforte hammer for the case when the hammer is rigid. He obtained the solution by the functional method of Kaufmann¹ considering the discontinuous changes in the pressure of the hammer due to the successive reflections of the impulse from the ends of the string. Prof. C. V. Raman and B. Banerji² obtained the solution of the same problem in a different manner by regarding the motion during impact as that of a loaded string. Mr. Das proceeded on a line similar to that given by Prof. Love³ for the longitudinal vibrations of a rod struck at the end.

The equation obtained by Mr. Das for the pressure exerted by the hammer is

$$F = 2\rho v_0 \left[e^{-kct} + e^{-k(ct-2a)} \left\{ 1 - k(ct-2a) \right\} + e^{-k(ct-4a)} \left\{ 1 - 2k(ct-4a) + \frac{k^2}{2!} (ct-4a)^2 \right\} \right] \quad (1)$$

¹ Ann. der Physik, Vol 54 (1895)

² Proc Roy Soc A, Vol 97 (1920)

³ Love's "Theory of Elasticity," p 411, Art 281 (2nd Edn)

where

ρ = the linear density of the string

m = the mass of the hammer

$h = 2\rho_0 v_0$

c = velocity of propagation of transverse wave on the string

v_0 = the initial velocity of the hammer

a = the distance of the striking point from the nearer end

t = variable time

He considered the total duration of contact of the hammer as divided up into a series of epochs determined by $0 < ct < 2a$, $2a < ct < 4a$, $4a < ct < 6a$ and so on, so that each of these epochs corresponds to the time taken by a pulse starting from the striking point in returning to the striking point after reflection from the nearer end¹. Thus the pressures in the successive epochs are —

$$\left. \begin{aligned} F_1 &= 2\rho_0 v_0 c e^{-hct} \\ F_2 &= 2\rho_0 v_0 c \left[e^{-hct} + e^{-h(c t - 2a)} \left\{ 1 - h(c t - 2a) \right\} \right] \\ F_3 &= 2\rho_0 v_0 c \left[e^{-hct} + e^{-h(c t - 2a)} \left\{ 1 - h(c t - 2a) \right\} \right. \\ &\quad \left. + e^{-h(c t - 4a)} \left\{ 1 - 2h(c t - 4a) + \frac{h^2}{2!} (c t - 4a)^2 \right\} \right] \end{aligned} \right\} \quad (2)$$

It will thus be seen, that at the end of every epoch, the pressure increases by a sudden jump of magnitude $2\rho_0 v_0 c$. Now we can determine the amplitudes of the different harmonics if we know the nature of the force acting on the string. For if F be the force acting on the string at a point distant a from one end, then using the notation adopted in Art. 130 of Lord Rayleigh's 'Theory of Sound,' Vol. 1, we find

¹ In his work Mr. Das considered reflection from the nearer end only, as the hammer leaves the string before the reflected pulse from the farther end reaches it—a supposition which is valid only for striking points near the ends.

that the amplitudes of the different harmonics are given by

$$\phi_n = \frac{2}{\pi n \rho} \sin \frac{\pi n}{l} \int_0^t F \sin n\pi(t-t') dt'$$

where the integration is to be made over the whole duration of contact. Thus we can proceed to calculate the amplitudes of the different harmonics by substituting for F the value given by the equation. In the present paper it will be shown that the amplitudes of the different harmonics as calculated from the equation agree with those found experimentally.

2 *The calculation of the amplitudes of the different harmonics.*

In order to calculate the amplitudes of the different harmonics we have to integrate the pressure equation over the whole of the duration of contact of the hammer with the string. But as the actual integration of the equation involves considerable mathematical labour, a mechanical and graphical method was employed in the integration of equation (3) given above, which considerably simplified the calculation. The method followed is that given below.

The pressures at successive epochs given by equation (2) are plotted against time, thus giving the variation of pressure of the hammer with time throughout the whole of the duration of contact of the hammer—(the point where the curve cuts the axis of time gives the duration of contact). Now since the magnitude of the discontinuous change in the pressure exerted by the hammer is the same at the end of each epoch, the plotting of the pressure-time curve is much simplified by calculating the initial discontinuity and the pressures at the end of every epoch at which the pressure suffers a sudden discontinuous change, and joining the intermediate portions for which the pressure decreases continuously by a continuous

straight line. The error committed in this way is very small as the actual curve differs very little from a straight line. Thus, at the time $t=0$, the pressure suddenly increases to $2\rho v_0 c$, and then continuously decreases until the reflected pulse from the end arrives at the hammer which takes place at the time $ct=2a$, when the pressure again increases suddenly by the same amount, *viz.*, $2\rho v_0 c$. Just at the end of the first epoch, *i.e.*, at the time $ct=2a$, the pressure is $F_1=2\rho v_0 c e^{-\lambda ct}$ and then suddenly increases by an amount equal to $2\rho v_0 c$, and again falls off continuously until the second reflected pulse reaches it, which takes place at the end of the time $ct=4a$, when it again increases discontinuously by the same amount, and again falls off continuously until the third reflected pulse reaches it, and so on, till the impact ceases. Having obtained the pressure time curve between the time $t=0$ to the time when the curve cuts the axis of time, we proceed to calculate the value of the expression

$$\phi_s = -\frac{2}{\pi c \rho} \sin \frac{\pi a}{l} \int_0^t F \sin n(t-t') dt'$$

Now the expression inside the integral sign can be broken up into two expressions

$$\int_0^t F \sin n(t-t') dt' = \int_0^t F \sin nt \cos nt' dt' - \int_0^t F \cos nt \sin nt' dt'$$

and taking $\sin nt$ and $\cos nt$ outside the integral sign, the expression for ϕ_s becomes

$$\phi_s = \frac{2}{\pi c \rho} \sin \frac{\pi a}{l} \left[\sin nt \int_0^t F \cos nt' dt' - \cos nt \int_0^t F \sin nt' dt' \right] \quad (4)$$

Thus to calculate the values of ϕ , we multiply each ordinate of the pressure-time graph by $\cos nt'$ and $\sin nt'$ respectively and obtain two new curves with these values as ordinates. The areas of these curves between the origin and the point where they cut the axis of time give the values of the two integrals in equation (4). The areas of these curves were measured by means of a planimeter and the amplitudes of the different harmonics were obtained by putting $s=1, 2, 3$, etc., respectively. In the numerical computation, those values of ρ, v_0, c and λ were used which were afterwards employed in the experimental determination described below. The calculated values of the amplitudes up to the tenth harmonic are given in Tables I and II for two different striking points, *viz.*, $l/10$ and $l/9$.

3. *Experimental determination of the amplitudes of the different harmonics*

An experimental verification of the above results was attempted in the following way. A steel wire 150 cm. long was stretched over the bridges fixed on the table. The linear density of the wire was .081 grm per centimetre. A mechanical hammering arrangement was made by mounting a small solid brass cylinder at the end of a light pivoted shaft, which could be caused to impinge transversely on the wire. The effective mass of the hammer used was 20.5 grammes. The amplitudes of the different harmonics were measured by means of an observing microscope. For measuring the amplitude of the fundamental, the microscope was focussed on the middle of the string and the hammer was caused to strike at the points for which the calculations were made, *viz.*, $l/10$ and $l/9$ respectively. To measure the amplitude of the octave, the microscope was focussed at $l/4$, and the string was damped at the middle immediately after the impact so as to stop the fundamental. Similarly, for other harmonics the string was damped at the corresponding node immediately *after* impact,

and observed at an antinode. The different amplitudes as measured by the microscope were then corrected for the amplitudes of other harmonics for which the point of observation is also an antinode. Thus from the measured amplitude of the fundamental were subtracted those of the 3rd, 5th and so on, similarly for others. In the following tables are given the observed values of the amplitudes of the different harmonics along with those calculated from the equation for two different striking points, *viz*, $l/10$ and $l/9$. The measurements were made up to the tenth harmonic for both the striking points

TABLE I.

Striking point at $l/10$

Harmonics	Observed amplitudes	Calculated amplitudes
Fundamental	3700 cm	3975 cm
Octave	0588 "	0593 "
Third	0433 "	0433 "
Fourth	0130 "	0131 "
Fifth	0078 "	0079 "
Sixth	0100 "	0117 "
Seventh	0020 "	0022 "
Eighth	0157 "	0173 "
Ninth	00112 "	00128 "
Tenth	0 "	0 "

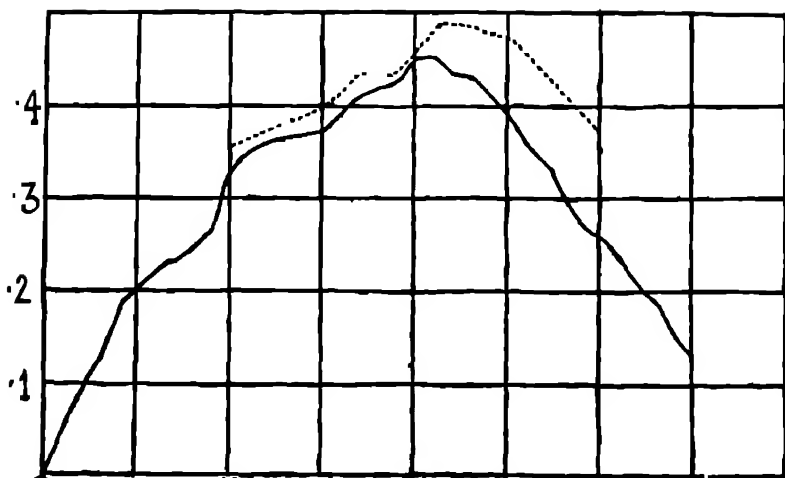
TABLE II.
Striking point 1/9.

Harmonics	Observed amplitudes	Calculated amplitudes
Fundamental	4.40 cm	4.22 cm
Octave	0.45 "	0.65 "
Third	0.67 "	0.73 "
Fourth	0.217 "	0.240 "
Fifth	0.046 "	0.043 "
Sixth	0.029 "	0.027 "
Seventh	0.071 "	0.068 "
Eighth	0.020 "	0.023 "
Ninth	0	0
Tenth	0.022 "	0.025 "

1 Variation of the amplitudes of the different harmonics with the striking point

In order to test the equation more fully, the amplitudes of the fundamental were determined for different striking points along the string both from the equation as well as experimentally. Theoretical calculations were made for seven different striking points along the string, *viz*, $1/15$, $1/10$, $1/9$, $1/8$, $1/7$, $1/6$ and $1/5$. Beyond the point $1/5$ the equation does not hold good, as the reflected pulses from the other end arrive at the hammer before it leaves the string, of which no account is taken in Mr Das's equation. Experimental determination was made up to the point $1/5$ of the string at an interval of 1 cm. The result is shown graphically in Fig 1.

Fig. I



The dotted curve gives the theoretical results whilst the continuous curve represents the experimental values. In Figs. II and III are given the curves showing the amplitudes of the octave and the third harmonic for different striking points along the string up to the middle point obtained experimentally. The ordinates are the amplitudes, and the abscissae are the distances of the striking point from the end.

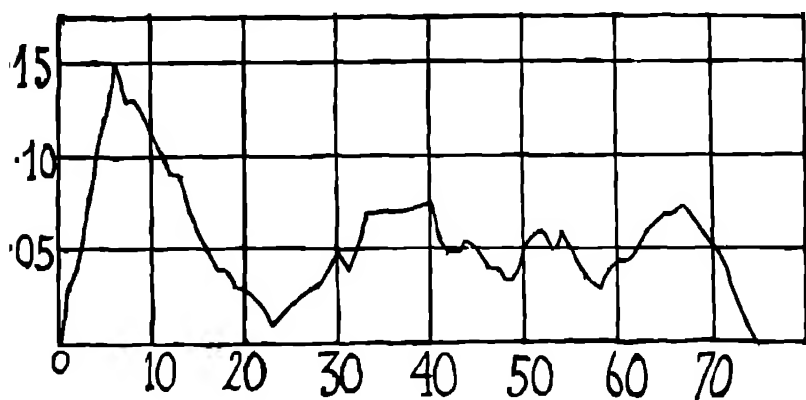


Fig. II

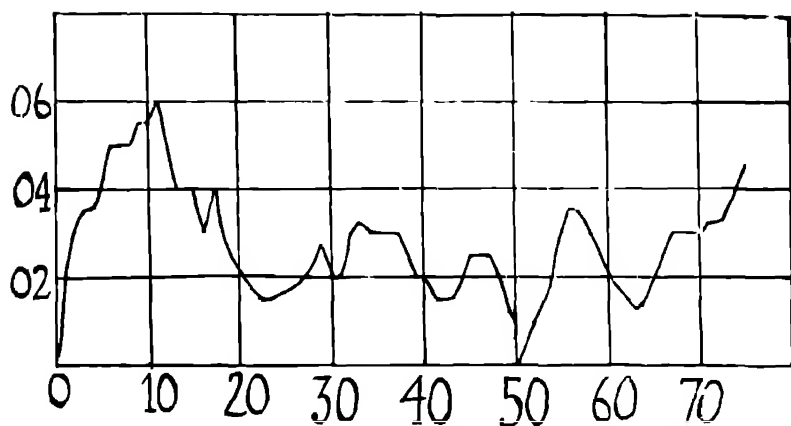


Fig. III

5 Conclusion

The very close agreement between the observed and the calculated values as seen from the above tables is a very good confirmation of the equation. It is also seen from the above tables that the observed amplitudes are always less than the calculated ones, a fact which follows from theoretical considerations. For, some amount of dissipation of energy takes place in the system of which no account is taken in Mr Das's theory. Moreover some allowance must be made for the fact that a certain time elapses, however small that may be, between the striking of the hammer and the measurement by the microscope, the effect of which is to lower the observed values.

It is seen from the curve showing the variation of amplitudes of the fundamental with striking point, that near about the point $l/7$ the amplitude of the fundamental is a maximum. Now in an actual pianoforte the choice of striking point is generally made at about the same point, *viz.* $l/7$. This may be due to the fact that the amplitude is a maximum at this point. The reason for this fact is that beyond this point the $\sin nt'$ and $\cos nt'$ terms in the integrals

change sign and so a part of the curve comes on the negative side of the time axis. At this point the value of the duration of contact becomes nearly $\frac{1}{4}$ th of the period of the string. The position of the striking point for which the amplitude of the fundamental is a maximum also depends on the mass of the hammer. As the weight of the hammer increases the point of maximum is shifted towards the end.

The rapid recovery of the amplitude of a harmonic as the striking point is moved away from one of its nodes is markedly shown in the results of the investigation.

The calculations have been made up to the point $l/5$, for beyond this we have to take into account the reflections from both ends which I hope to do in a later paper.

Further investigations as to the duration of contact and the effect of elasticity of the hammer are now in progress and will be given in a later paper.

The investigation here described was carried out in the Palit Laboratory at the University College of Science at the suggestion of Prof C V Raman, Palit Professor of Physics, and the author is indebted to him for the unfailing interest he has taken during the progress of the work.

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DEPARTMENT OF PHYSICS,

92, Upper Circular Road, Calcutta

1st May, 1923

VIII. On the Temperature Variation of the Electrical Conductivity of Copper and Iron fused with Mica.

By

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Three years ago, there was published in the Philosophical Magazine¹ a paper by A. L. Williams and Miss Mackey containing the results of some experiments on the electrical conductivity of mixtures of copper and iron with mica. The most remarkable feature about them was the very large variation of conductivity with temperature.

In Part B of the above paper are given the resistances of two samples each of copper-mica and iron-mica mixtures as measured by Miss Mackey. In all these, I find that the variation of resistance with temperature is expressed over the whole range of the experiment with a fair degree of accuracy by means of either of the formulae

$$R = PT^{-1} e^{Q/T} \quad (1)$$

$$\text{or} \quad R = P_1 T^{-1.2} e^{Q_1/T} \quad (2)$$

where R = resistance of the sample

T = temperature measured on the absolute centigrade scale and P, Q, P_1, Q_1 are constants

¹ Phil Mag, Vol XL, 1920, p 281.

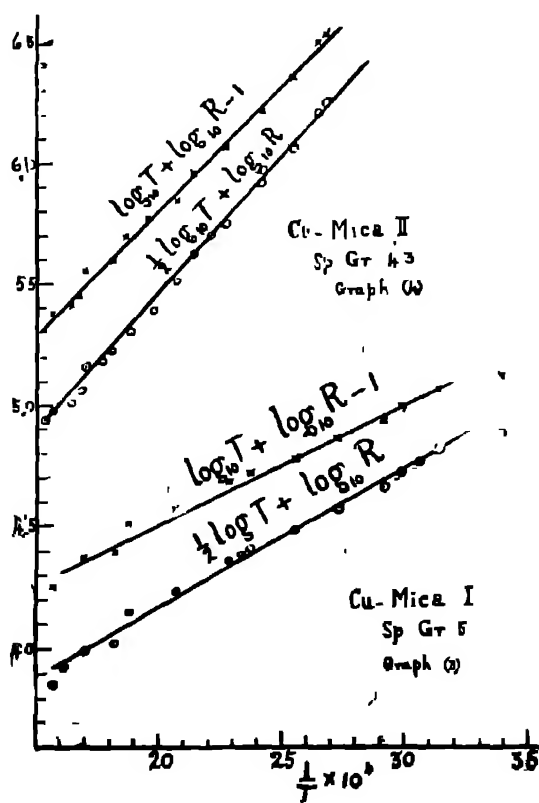
Taking logarithms,

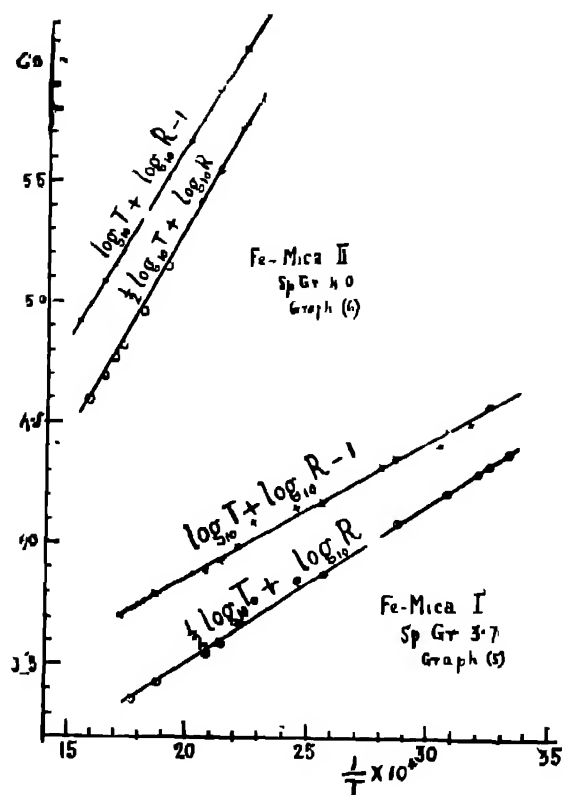
$$\log_{10} R + \log_{10} T = \log_{10} P + \frac{Q}{2 \cdot 303 T}$$

and

$$\log_{10} R + \frac{1}{2} \log_{10} T = \log_{10} P_1 + \frac{Q_1}{2 \cdot 303 T}$$

The quantities $\log_{10} R + \log_{10} T$ and $\log_{10} R + \frac{1}{2} \log_{10} T$ are plotted against T^{-1} in graphs 3 to 6, and the graphs are straight lines.





(The graphs have been given the same numbers as in Miss Mackey's paper)

Since the samples used were irregular, their specific resistances could not be determined and there is no significance in calculating the values of P and P_1 . In the following table are given the values of Q and Q_1 for the different specimens

Specimens	'p gr	Q	Q_1
Cu-mica I	5.1	1.27×10^3	1.13×10^3
Cu-mica II	4.3	2.63×10^3	2.96×10^3
Fe-mica I	3.7	1.50×10^3	1.30×10^3
Fe-mica II	4.0	4.01×10^3	3.78×10^3

It will be noted that Q and Q_1 show a decrease with increasing metal content in Cu-mica and an increase with increasing metal content in Fe-mica.

Theoretical.

The expression $R = PT^{-1} e^{Q/T}$ can be put into the form $\sigma = P^{-1} T e^{-Q/T}$ where σ is the conductivity of the sample. This is of the same form as the expression for the variation of the number of thermions in equilibrium with a metal in a vacuum enclosure

$$n = A T^\lambda e^{-b/T} \quad (1)$$

where λ is a constant which may be given any value between 0 and $\frac{1}{2}$ without appreciable difference (O. W. Richardson, *Emission of Electricity from Hot Bodies*, Chap. III). Assuming the concentration of free electrons in the mixture to vary in a similar manner with temperature, we can calculate the variation of conductivity with temperature. On the electron theory of metallic conduction,

$$\sigma \propto \frac{n e^2 l}{T}$$

where

n = number of free electrons per unit volume

v = root mean square of the velocity of electrons

l = mean free path of the electron

and

e = electronic charge

Since

$$v \propto T^{1/2}$$

$$\sigma \propto n e^2 l / T^{1/2}$$

If we assume that l is independent of temperature, and n varies with temperature according to equation (3)

$$\sigma \propto T^{\lambda - \frac{1}{2}} e^{-b/T}$$

If $\lambda = \frac{1}{2}$

$$\sigma \propto T e^{-b/l}$$

and if $\lambda = 1$

$$\sigma \propto T^{\frac{1}{2}} e^{-b/T}$$

Since writing the above note, there has appeared in the Journal of the Franklin Institute a paper on the "Resistivity of vitreous materials" by L. L. Holladay where the author has put forward the same type of formula to explain the variation of the resistivity of a number of specimens of glass with temperature. It is of interest to compare the values of Q for the glasses and the metal-mica mixtures. The values calculated by Holladay for the glasses range for different specimens from 9.37×10^4 to 1.30×10^4 and are thus of the same order of quantities as those calculated for the metal-mica mixtures.



Fig. II

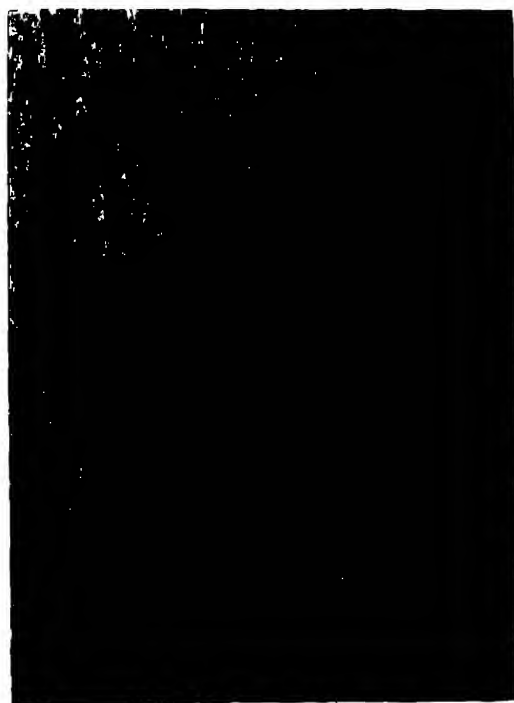
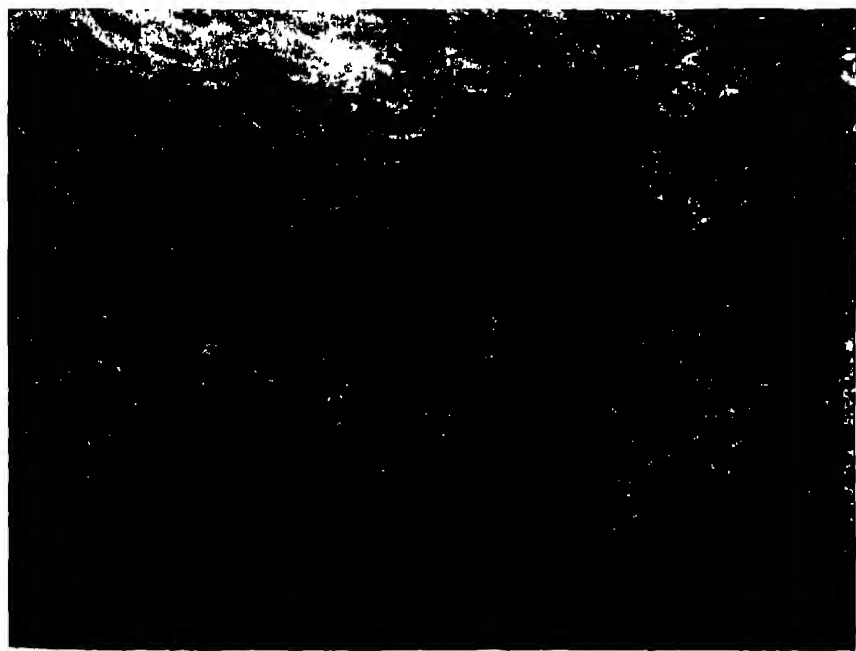


Fig. I



IX. Effect of Barriers on Ripple-Mark

By

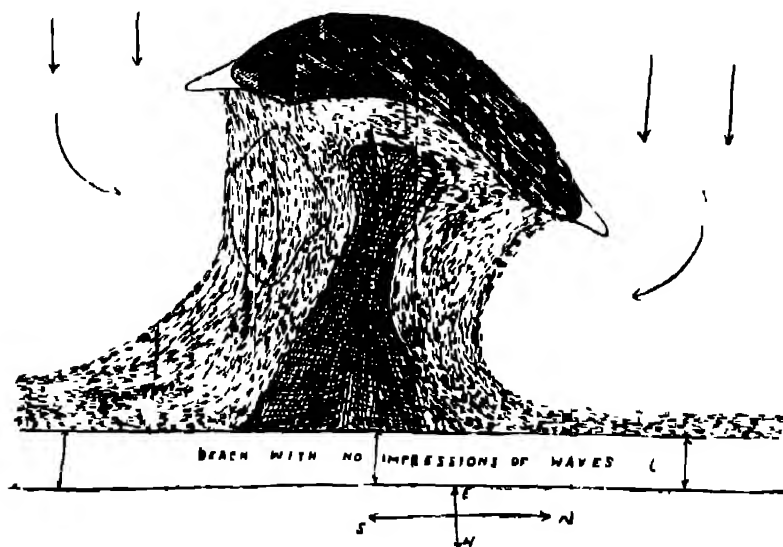
S K BANERJI, D.Sc.,

Director, Bombay and Alibag Observatories

[Plates III and IV]

I had on many previous occasions examined theoretically the effect of various types of barriers on a set of plane waves. But little did I expect then to see the effects of barriers on wave motion manifested on such a magnificent scale as I have recently done during my stay at Alibag. The sea beach in front of the magnetic observatory at Alibag has a very little slope hardly more than 7° . The sand is of such a fine quality that it easily catches impressions of waves. The impressions are in the forms of ridges and hollows all regularly arranged parallel to the wave-fronts. They are formed during high tides and are left behind when the sea retires.

In front of the beach at Alibag there is an old fort which acts as a barrier to the advancing sea-waves during high tides. The effective length of the fort acting as a barrier is



nearly 300 yards and during high tide an equivalent length behind the fort is covered with water, this length of course varying according to the day of the lunar month and the order of the tide. But when the sea retires, nothing but a set of impressions of the waves is left behind the fort on the fine sand with perhaps a small quantity of water here and there clogged in the hollows between the ridges.

A certain minimum head of water appears to be necessary in order that the sand may catch impressions of waves. As a consequence of this a certain portion of the beach measured from the highest point wetted by the water remains almost a plane without any impression. But beyond this the whole of the beach exposed during ebb-tide (and it is quite possible that a portion of the beach still beneath water) is marked by a conspicuous set of ridges and hollows. In the open beach these arrange themselves parallel to the wave front in a perfectly regular manner. A photograph of the impressions on the open beach is given in Fig I, Pl III.

The effect of the barrier on the waves is however the most interesting. The sets of parallel ridges on the open beach curve round as we come behind the barrier, and as we approach it they become deformed and curly in appearance and meet the edge of the barrier inclined at definite angles to it. This edge-effect is shown in Fig II, Pl. III. In the central region just behind the barrier, the ridges again arrange themselves in a regular manner parallel to the barrier. The wave systems in this region approach the barrier almost normally to it and are reflected as such. This is clearly shown in Fig. I, Pl. IV. As we move from the barrier towards the shore, the ridges gradually lose their regularity and a well-defined region of very complex impressions is easily recognised. These complex impressions appear to be produced by the meeting of the succession of waves coming from either side. A sample of the complex impressions is shown in Fig. II, Pl. IV.

It should be remembered that a set of tidal waves approaching a sloping beach usually breaks and moves forward as a 'rolling' wave. If we conceive of a set of waves approaching a sloping beach in succession, then we can easily picture to ourselves that by the time the second wave arrives, the first will have gone up the beach to the maximum extent and begun to retrace its steps and met the second half-way, giving a backward push to the lower portion of this wave, while the crest will still maintain its forward velocity. In consequence, it will break and appear to move as a rolling wave. It is not usually the second wave that breaks, but breaking may take place at a much earlier stage on account of the continuous downward flow of water during the return journey maintained by the succession of advancing waves. Owing to this complexity no mathematical form can be assumed for these waves. But if the slope of the beach is neglected and the advancing waves be assumed to have their elevation varying as simple harmonic function of the time the general features of the sand impressions formed behind the barrier at Alibag are easily explained from theoretical considerations.

A rough drawing of the impressions formed on the sand has been made after a careful examination of them as they were actually found. This is reproduced above in the text.

X. The Diffraction of X-rays in Liquids, Liquid Mixtures, Solutions, Fluid Crystals and Amorphous Solids.

By

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- 1 Introduction
- 2 Comparison with the optical scattering problem
- 3 X-ray scattering at very small angles with the primary beam
- 4 Explanation of the X-ray diffraction-halo of liquids.
- 5 Analysis of molecular positions in a liquid and in mixtures and solutions
- 6 Calculation of the intensity of X-ray scattering.
- 7 Comparison with observations
8. Liquid crystals
- 9 Amorphous solids
10. Summary and conclusion

1. Introduction.

When a narrow pencil of homogeneous X-rays passes through a thin layer of liquid and is received on a photographic plate, it is found that with a sufficient exposure, besides the central spot given by the undeviated pencil, there appears on the plate also a circular diffraction halo surrounding the

¹ A preliminary note in which the theory developed in this paper was indicated appeared in "Nature," Feb 10, 1923, p 185

centre and separated from it by a relatively clear space. This somewhat surprising observation was made by Debye and Scherrer¹ in the course of their work on X-ray diffraction. The same result has also been obtained in some recent X-ray studies by Hewlett² in which the ionization method was employed. Keesom and Smedt³ have also studied the phenomenon in the case of several liquids by the photographic method and find that in some cases there is a weak second halo outside the first and even the suspicion of a third.

The behaviour in this respect of the special class of substances known as liquid crystals and studied by Lehmann and others is obviously of much interest. At the suggestion of Prof. Debye, observations were made by Hückel⁴ with several of these substances, particularly with p-azoxyanisol and cholesteryl-propionate which were studied in (1) the solid crystalline, (2) the liquid crystalline, and (3) the liquid isotropic conditions. In the solid crystalline state, several sharp rings similar to those of other crystal powders were obtained, but remarkably enough, there was no notable difference shown by the photographs obtained with the isotropic and crystalline liquid states. In both cases a single diffraction halo appeared as in the case of ordinary liquids. It may also be mentioned that observations by Friedrich⁵ on the scattering of X-rays by wax and other amorphous solids and by Jauncey⁶ on the scattering by glass similarly show a maximum at a considerable angular distance from the undeviated pencil. It thus appears that in the three cases of an isotropic liquid, of a liquid crystal, and of an amorphous solid, we have essentially similar phenomena exhibited.

¹ Nachrichten Göttingen, 1916

² C. W. Hewlett Physical Review, XX, 1922, p. 688

³ Keesom and Smedt Proc. Roy. Soc. Amsterdam, XXV, 1922, p. 118, and XXVI, 1923, p. 112

⁴ Hückel, Phys. Zeit., 1921, p. 561

⁵ Friedrich Phys. Zeit., 14, 1913, p. 317

⁶ Jauncey Phys. Review, XX, 1922, p. 405,

From the survey of the literature, it would appear that no satisfactory explanation of the appearance of the diffraction halo in these cases has so far been put forward. One view that has been suggested¹ is that the halo might be a diffraction-effect arising from the finite size of the molecule or the co-operation of the different atoms in it. This suggestion however must be negatived in view of Keesom and Smedt's observation that a liquid like argon which presumably has monatomic molecules shows the phenomenon in much the same degree as substances with more complex molecules. Another view that has been put forward by Hewlett² is that ordinary liquids possess something resembling crystal structure. The idea that in a liquid there are large groups of regularly arranged atoms is also put forward by A. H. Compton³ in his recent report on X-ray scattering, when referring to observations by Hewlett and Duane. These hypotheses by Hewlett and Compton appear to us to be somewhat artificial; they have obviously been introduced in order to explain the observed effects, but lack independent justification. Keesom and Smedt have attempted to interpret their results as due to the interference of the effects of two neighbouring molecules, using for this purpose a formula proposed by Ehrenfest. Their theory, however, appears to us inadequate. The essential features of the phenomenon are the region of the relatively very small intensity of scattering surrounding the central spot, and beyond this a moderately sharp diffraction-halo, having a much greater intensity than the scattering at large angles. Neither of these features is indicated by Ehrenfest's formula. To make the point clear we give below in Fig. 1C the curve of intensity for benzene reproduced from Hewlett's paper, and in Fig. 1A for comparison with it a graph of the intensity calculated from Ehrenfest's formula. It will be seen that

¹ Debye referred to by Hückel

² *Loc. cit.*

³ Bulletin, National Research Council, U. S. A., No. 20, p. 14.

there is little in common between them. Finally we should mention an attempt which has been made by L. Brillouin¹ to explain the phenomena of X-ray diffraction in liquids and amorphous solids on the basis of the quantum theory of specific heats. We give in Fig 1B a graph of the intensity in different directions drawn from his final formula. It will be seen that it bears no resemblance whatever to the observed result given in Fig. 1C.

We propose in this paper to approach the problem from an entirely different standpoint. In a series of publications² that have appeared in the course of the last two years, the authors and their co-workers have discussed the optical problem of the scattering of light in liquids under various conditions and shown that the experimental evidence amply confirms the

¹ *Annales de Physique*, Jan-Feb 1922, pp 88 122

² 1 Notes by C V Raman in *Nature*, November 10, 1921, and several subsequent issues

2 "Molecular Diffraction of Light" by C V Raman, *Calcutta University Press*, February, 1922

3. "The Molecular Scattering of Light in Water and the Colour of the Sea" by C V Raman, *Proc Roy Soc*, April 1922, pp 64-80

4 "The Molecular Scattering of Light in Vapours and in Liquids and its Relation to the Opalescence observed in the Critical State" by K R Ramanathan, *Proc Roy Soc*, Vol 102, 1922, pp 151 161

5 "The Molecular Scattering of Light in N pentane" by R Venkateswaran, *Trans Chem Soc.*, Vol 121, 1922, p 2655

6 "The Molecular Scattering of Light in Liquid Mixtures" by C V Raman and K R Ramanathan, *Phil Mag*, Jan 1923, pp 213-224

7 "The Molecular Scattering and Extinction of Light in Liquids and the Determination of the Avogadro Constant" by C V Raman and K S Rao, *Phil Mag*, March 1922 pp 635 640

8 "Electromagnetic Theory of Scattering of Light in Fluids" by K R Ramanathan, *Proc Ind Assn for the Cultivation of Science*, Vol VIII, Part I, pp 1-22

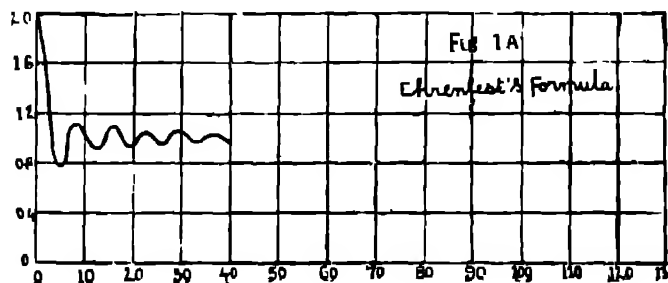
9. "The Visual and Photographic Albedo of the Earth," by K R Ramanathan, *Astrophysical Journal*, April, 1923.

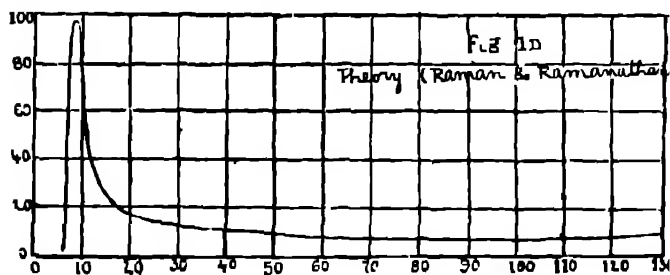
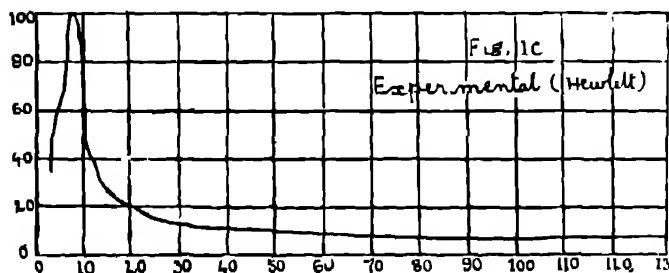
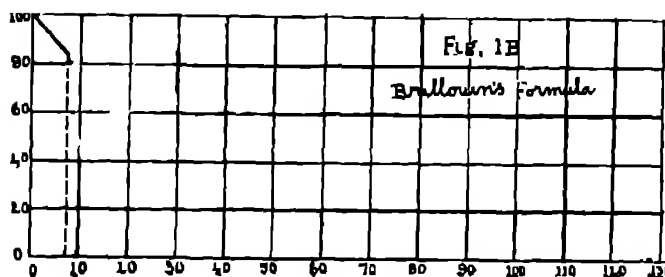
10 "The Molecular Scattering of Light in Benzene Liquid and Vapour" by K R. Ramanathan, appearing in the *Physical Review*, 1923

11 "The Molecular Scattering of Light in Liquid Mixtures" by J C Kamecwar Ray, appearing in the *Physical Review*, 1923

And other forthcoming papers

statistical-thermodynamical theory of light-scattering developed by Smoluchowski and Einstein. The essential idea of the Einstein-Smoluchowski method is to treat a fluid as a continuous substance subject to local changes of density determined by thermodynamical considerations. Leaving out of account the effects due to the anisotropy of the molecules, the theory leads in the optical case to precisely the same results as those given by a more explicitly molecular treatment. This is due to the circumstance that the length of light waves is vastly greater than the scale of molecular dimensions, and hence the assumption involved in treating the substance as a structureless continuum does not lead to any appreciable error. The case is different however when we deal with the problem of diffraction of X-rays. The wave-length here is less than the average distance apart of the molecules, and in applying the statistical-thermodynamical considerations developed by Smoluchowski and Einstein, we have explicitly to take into account the fact that the medium is not continuous, but consists of a finite number of discrete particles. When this is done, the experimental results are explained quantitatively in a satisfactory manner. Fig. 1D gives the graph of intensity calculated from the formula we have developed in this paper. When account is taken of the imperfect homogeneity of the X-rays used by Hewlett, it will be seen that his experimental curve reproduces with remarkable fidelity the indications of theory.

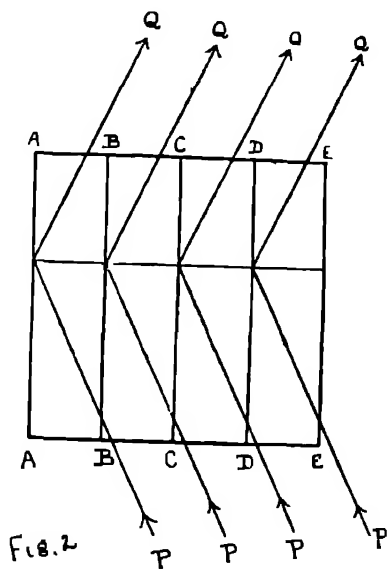




2. Comparison with the optical scattering problem.

In order more clearly to appreciate the relations between the optical and X-ray problems, it is desirable here to give a brief outline of the theory of the former case. In Fig 2, let ABCDE represent a unit volume of fluid (supposed of refractive index only slightly differing from unity) on which a parallel pencil of light is incident. Let n be the total number of molecules in it and let PPPP represent the in-falling rays and QQQQ the scattered rays in the particular direction under consideration. The volume ABCDE

may be divided into a very large number of slices by a series of equidistant planes perpendicular to the plane of the paper and equally inclined to the incident and scattered rays. It is assumed that each slice is thick enough to be several molecules deep and yet very thin compared with the wave length of the incident light. It is obvious that with these assumptions the scattered waves arising from the molecules in each slice may be taken to be all in identical phases. Let, A, B, C, D, etc be successive



planes which are situated at such intervals that the path differences of the scattered rays arising from layers adjacent to them differ by one wave-length. Each of the slabs AB, BC, etc., thus contains a considerable number, say r of the thin slices into which the medium was supposed to be divided. Then $AB = BC = CD = DE = \frac{\lambda}{2} \sin \frac{1}{2} \theta$ where θ is the angle of scattering and λ is the wave-length of the incident radiation. Since the effects of all the molecules in a given slice, say the p th, of any one slab are taken to be in the same phase, they also agree in phase with those from the p th slice of every

other slab. The amplitudes of the scattered waves arising from all the molecules lying in the p th slices of all the slabs may then be added up, and their resultant amplitude is proportional to the total number of molecules contained in the slices thus added together, denote this by n_p . The whole scattering may then be found by summing up the effects proportional to n_1, n_2, \dots, n_r , of the successive slices, due regard being had to their respective phases, which are distributed at regular intervals from 0 to 2π . If $n_1 = n_2 = \dots = n_r = n$, the effects of the different slices would completely extinguish each other by interference. This corresponds to the case of a completely homogeneous medium, that is, a crystal at the absolute zero of temperature for waves of length great compared with its grating constant. In every other case, n_1, n_2 , etc. would show fluctuations in value, and part of the incident energy would appear as scattered or internally reflected radiation. We know that $n_1 + n_2 + \dots + n_r = n$ and hence, denoting $n_1 - n/r = \Delta n_1$, $n_2 - n/r = \Delta n_2$, so on, the resulting effect would simply arise from the quantities $\Delta n_1, \Delta n_2$, etc. which represent the fluctuations from the mean density, the part due to the mean density itself disappearing by interference.

We can now consider the magnitude of the fluctuations $\Delta n_1, \Delta n_2$, etc. in different cases. We take first the case of an ideal gas which has been discussed by H. A. Lorentz.¹ Here the distribution of the molecules is a purely random one, and the average expectation of magnitude of the fluctuations $\Delta n_1, \Delta n_2$, etc. can be very simply shewn from probability considerations to be $\sqrt{n/r}$. If further, we make the assumption which is *a priori* justifiable in the case of an ideal gas—that the quantities $\Delta n_1, \Delta n_2$, etc. are as often positive as negative and vary quite independently of each other, then to find their aggregate effect, we add up *not* their amplitudes in their respective phases, but their intensities without regard to phase.

¹ Proc. Roy. Soc. Amsterdam, Vol. 13, 1910, p. 92

The total scattering will thus be proportional to $r(\sqrt{n}/r)$, or simply n , that is, to the total number of molecules in the fluid per unit of volume. This is the well-known Rayleigh law of scattering.

We next consider the case of a gas not obeying Boyle's law in which the distribution of molecules is no longer a random one. Here, applying Boltzmann's principle of entropy-probability, we find the mean value of Δn_x to be, $n \sqrt{R\beta T/N}$, where R and N are respectively the gas constant and Avogadro constant for a gram-molecule, T is the absolute temperature and β is the isothermal compressibility of the fluid. Assuming as in the case of an ideal gas that Δn_x , Δn_y , may be as often positive as negative, and that their values are quite independent of each other, we get the total scattering by squaring and adding their intensities. The net result is thus proportional to

$$n^2 RT\beta/N \quad (1)$$

and is thus proportional to the compressibility and to the absolute temperature and to the *square* of the density. For a gas obeying Boyle's law, β is the reciprocal of the pressure and it is easily seen that the expression reduces to n , which is the Rayleigh law of scattering.

For a liquid or very dense vapour of which the refractive index is sensibly greater than unity, the discussion proceeds on exactly the same lines as above, except that the local electromagnetic field due to the molecules themselves cannot be neglected in comparison with the field due to the incident wave and must be taken into account as in Lorentz's theory of dispersion. This increases the intensity of the scattered light without affecting its state of polarisation as shown in the paper (8) by Ramanathan quoted above. The scattering due to a unit volume is now proportional to

$$\left(\frac{\mu^2 + 2}{3}\right)^2 n^2 RT\beta/N \quad \dots \quad (2)$$

where μ is the refractive index of the fluid. When μ is sufficiently nearly equal to unity, (2) reduces to (1)

3. *X-ray scattering at very small angles with the primary beam.*

It will be seen that the simple treatment given above depends essentially on the possibility of dividing up the medium into slabs of thickness $\lambda/2\sin\frac{1}{2}\theta$ which can be further subdivided into several slices, each of which is many molecules thick, so that the fluctuations of density in any slice can be assumed to be independent of those in neighbouring ones. This, in general, is obviously possible only when λ is large, which is true in the optical case. When λ is comparable with molecular dimensions, and θ has any moderate value, each slab of thickness $\lambda/2\sin\frac{1}{2}\theta$ would be only a few molecules thick, and it would no longer be possible to assume that when it is sub-divided into thinner slices, the fluctuations in the different slices are uncorrelated, *i.e.*, independent of each other. In fact, it is easy to see that when the volume of the liquid is divided into very thin slices each only a molecule or so in thickness, any excess of density in one slice necessarily involves a deficiency in the adjoining slices and *vice-versa*. The simple summation of the intensities of the scattered waves due to the density-fluctuations in the different slices, thus ceases to be admissible.

In one case, however, the Einstein-Smoluchowski theory may be applied as it stands to the problem of X-ray scattering. This is when the angle of scattering θ is very small. The thickness $\lambda/2\sin\frac{1}{2}\theta$ of the slabs AB, BC, CD, is then appreciable and may be made as large as we please by sufficiently decreasing θ . For instance if $\lambda = 0.71$ A. U., and $\theta = 10'$ of arc, $\lambda/2\sin\frac{1}{2}\theta = 239$ A. U. and each of the slabs AB, BC, etc., would, if we take the case of benzene liquid, be about 50 molecules thick. This thickness should be ample to enable the Einstein-

Smoluchowski theory to be applied. The isothermal compressibility β being 90×10^{-12} dynes per cm^2 for benzene, it is easily shown by calculation that the scattering given by formula (1) is $1/40$ times smaller than in proportion to the number of molecules per unit volume. The scattering of X-rays at these small angles by liquids is thus almost negligible. Even for an angle of scattering of 2 degrees, a layer $\lambda/2\sin\frac{1}{2}\theta$ thick would be about 5 molecules deep, and though the Einstein-Smoluchowski theory would not be strictly valid, it could still be applied as a rough approximation, and the result indicated, *viz.*, that the scattering is very small would hold good.

It is thus seen to be a simple consequence of thermodynamics that in respect of scattering of X-rays through small angles, ordinary liquids stand in a position not very dissimilar to that of a complete crystal or of a crystal powder. The principal point of difference is that, in crystals, the compressibility is even smaller than in liquids and the scattering at small angles is therefore practically evanescent.

4. Explanation of the X-ray diffraction-halo of liquids.

As the angle of scattering θ is gradually increased, a stage is arrived at when the slab $\lambda/2\sin\frac{1}{2}\theta$ is only one or two molecules thick, and it is clear that the thermodynamical theory based on the idea that the fluid is a structureless continuum must then be modified. The essentially new feature that must be taken into account is that the fluctuations of density in neighbouring slices are no longer uncorrelated. Without going very deeply into the mathematical theory, it is easy to understand in a general way the nature of the results to be expected. For simplicity, we shall consider the case of a liquid which has only a very small compressibility, and in which consequently the thermal fluctuations of density are very small; this means again that the molecules tend to be distributed in space in a manner approaching uniformity,

and not chaotically as in a gas. If, as before, there be n molecules per unit of volume, it is convenient to regard as the mean molecular distance a length λ_0 given by the formula

$$\lambda_0 = kn^{-1/3}$$

where k is a number of the order of magnitude of unity; regarding the exact value of k , we shall have more to say hereafter. Further, let the angle of scattering θ be such that $\lambda = 2\lambda_0 \sin \frac{1}{2}\theta$. Then each of the slabs AB, BC, etc., would on the average be just one molecule thick. It is obvious that in such a case, as has already been remarked, the supposition that when each slab is further subdivided into a number of slices, the effects of the molecules contained in the different slices would practically cut each other out by interference, would be entirely wide of the mark. In the first place, the number of the molecules in the different slices, would show fluctuations of *relatively* considerable magnitude. Further, instead of these fluctuations of density being entirely uncorrelated, they would be almost completely correlated in the direction of amplifying the total observed effect. For assuming that out of the r slices into which the slab AB is divided, the middle slice contains at any instant an excess number of molecules, the chance that at the same instant the slices near the face A or B contain a corresponding deficiency in molecules is very large. Since the scattered waves due to molecules in the middle and the outer faces of the slab differ in path by $\lambda/2$, the effects due to the excess in one slice and the deficiency in the others, would have *identical* phases, and their amplitudes would thus add up. Thus a very large scattering may be expected in the direction referred to, in fact many times greater than if the different molecules were regarded as scattering centres in random distribution of phase.

Theory thus leads us to expect a very large scattering in the direction θ where $\lambda = 2\lambda_0 \sin \frac{1}{2}\theta$, λ_0 being the mean molecular distance. Since as we have seen, the scattering is almost

nothing at small angles, it follows it should increase rather abruptly as θ increases and approaches the value $2 \sin^{-1} \lambda / 2\lambda_0$. On the other hand, when θ reaches and passes this special value, we should expect a fall of intensity which is somewhat less rapid. For, as the angle of scattering is increased, the quantity $2\lambda_0 \sin \frac{1}{2}\theta$ becomes greater than λ , and hence the fluctuations of density in the different slices begin to neutralise each other's effects by interference, but not perfectly, owing to the want of correlation. At large angles, a considerable effect would be left over as the result of this incomplete correlation, and this may be expected to be still much greater than the Einstein scattering obtained in directions nearly parallel to the primary beam.

The theory thus clearly indicates that the diffraction-halo should be fairly sharp at its inner edge, and rather diffuse at its outer margin. These features are well shown in Hewlett's ionisation curves and Huckel's photographs already cited.

5 Analysis of molecular positions in a liquid and in mixtures and solutions

In order to present the theory of the X-ray diffraction-halo exhibited by liquids as outlined above in a more complete mathematical form, we have to see how the theory of density-fluctuations which is based on the idea that a fluid may be regarded as a continuum should be modified so as to take into account its actual coarse-grained structure. From general thermodynamical considerations, it is clear that the distribution of the molecules in any small volume of liquid can neither be absolutely uniform and geometrically regular and periodic as in a perfect crystal, or absolutely chaotic as in an ideal gas. The character of the distribution as influenced by the thermal agitation and other factors must in fact be intermediate between these two extreme types. The density of matter present must fluctuate

from place to place and these fluctuations of density may be viewed in two rather different aspects. The first way of regarding them is that adopted by Einstein and Smoluchowski, that is, to ignore the independent existence of discrete molecules and confine attention to the total quantity of matter present in volumes which are small enough to be beyond the limit of microscopic observation, but large enough to contain a great number of molecules. This is quite sufficient for the purpose of dealing with the optical problem and also the X-ray scattering at very small angles. The second way of regarding the matter is to take cognisance of the individual molecules and of their movements in order to discuss and analyse the fine structure of the liquid, and this is necessary when we discuss the scattering of X-rays at larger angles. When we consider the fluctuations of density from the first point of view, their magnitude may be predicted completely from a knowledge of the compressibility of the matter in bulk, and it is unnecessary to know either the weight of the molecules or their size and shape. The fine structure of the liquid on the other hand can only be fully determined if we know the properties of the individual molecules. The thermal agitation is one of the factors that must be considered in carrying out this analysis of the positions of the molecules in any state of aggregation of matter, but that it is not the only factor is a fairly obvious proposition. To realise this, we have only to recall the extreme case of a crystal at the absolute zero of temperature. Here we have no "thermal" fluctuations of density, but the structure exhibits complex periodic fluctuations of density that do not vary with time.

As a preliminary to the more complete analysis of positions of molecules in a liquid, we shall first set out clearly the theory of density-fluctuations in a liquid in the simpler form sufficient for the optical problem.

Thermal fluctuations of density: Let us assume that the fluid is enclosed in a cube of edge-length L each way in the

fluid, the co-ordinates of any point within this volume lying between the limits

$$0 < x < L$$

$$0 < y < L$$

$$0 < z < L$$

Let the density of the liquid in any small region be denoted by

$$\rho, \text{ where } \rho = \rho_0 + \Delta$$

ρ_0 being the average density, and Δ the fluctuation. The work done in compressing the fluid contained in any small volume V so that its density is increased by Δ is

$$\frac{1}{2} \cdot \frac{1}{\beta} \left(\frac{\Delta}{\rho_0} \right)^2 V$$

and putting this equal to

$$\frac{1}{2} R T / N,$$

we get at once for the mean square of the fluctuation

$$\Delta^2 = \rho_0^2 \cdot R T / N V$$

The same result may also be derived by assuming that the medium is traversed by plane sound-waves of different wavelengths, whose energy is distributed in accordance with the equipartition principle. Following Einstein,¹ we may write

$$\Delta = \sum_l \sum_m \sum_n B_{lmn} \cos 2\pi l \frac{x}{2L} \cos 2\pi m \frac{y}{2L} \cos 2\pi n \frac{z}{2L}$$

where l, m, n , are positive integers. The potential energy in the sound-wave whose amplitude is B_{lmn} , when integrated over the volume V , is easily shown to be

$$\frac{L^3}{16} \cdot \frac{B_{lmn}^2}{\rho_0^2} \cdot \frac{1}{\beta}$$

¹ *Annalen der Physik*, 1910, Band 33, p. 1283.

The law of distribution of each B_{lm} is thus

$$C \exp \left\{ \frac{-N}{RT} \frac{l^2}{16} - \frac{B_{lm}^2}{\rho_0^2} \right\} d B_{lm}$$

where C is a constant, and it follows that the mean value

$$\bar{B}_{lm}^2 = \rho_0^2 \cdot RT\beta/Nl^2$$

which is identical with that given above, since

$$\Delta^2 = \bar{B}_{lm}^2$$

This method of analysing the irregular distribution of molecules in a fluid into a system of sound-waves in a continuous medium is of course merely a convenient mathematical artifice. Einstein adopts it in his paper and shows that for each given direction, it is sound-waves of a particular wave-length that are chiefly responsible for the scattering of light; this wave-length λ_1 is connected with the angle of scattering θ and the wave-length of the light λ inside the fluid by the formula

$$\lambda = 2 \lambda_1 \sin \frac{1}{2} \theta$$

The wave-length of the sound waves which are chiefly effective is thus, except for very small angles of scattering, of the same order of magnitude as the wave-length of the incident radiation.

In order that the thermal energy of the fluid may be identified with the energy of propagation of sound waves in it, it must, as is well-known, be assumed that the sound-wave spectrum is limited on the short wave-length side, the smallest permissible wave-length λ_s being given by the expression

$$\lambda_s = n^{-\frac{1}{2}} \cdot \sqrt{\frac{4\pi}{9}} = 1.118 n^{-\frac{1}{2}}$$

It is thus clear *prima facie* that Einstein's method of considering the problem of scattering must fail when the wave-length of the incident radiation and the direction of observation considered are such that the sound-waves chiefly responsible

for the scattering have a wave-length equal to or less than this limiting wave-length which is determined by the structure of the medium. We have already shown however, that even before this limit is reached, the influence of the discrete structure begins to be felt and the conception of sound-waves in a continuous medium ceases to be appropriate as a method of dealing with the scattering problem.

Analysis of Fine Structure of Liquids In the foregoing application of the Fourier analysis to the determination of the thermal fluctuations of density, it was tacitly assumed that apart from these fluctuations, the fluid itself could be regarded as a uniform continuum. This limitation must now be dispensed with, and the Fourier analysis applied to the determination of the actual distribution of matter in the fluid. The result of the analysis would depend on the manner in which the molecules, or rather the electrons in them responsible for the scattering of X-rays, are dispersed in space. If they formed a regular space-lattice—(this contingency cannot of course arise in any actual liquid)—the analysis would indicate a definite periodicity in the distribution of matter with wave-length equal to the grating constant of the lattice. Actually, of course, we cannot expect such sharply-defined periodicities or “structural line-spectra” in a liquid. We should rather expect to get as the result of the analysis, a “continuous structural spectrum” having its chief peak of intensity at a wave-length equal to or comparable with the mean distance between neighbouring molecules. We have to find a formula which will indicate the distribution of intensity in the “structural spectrum.” This cannot of course be done completely without a knowledge of the special characteristics of the molecules under discussion. But, by considering only the essential features of the case, it would appear that the problem can, at least approximately, be solved with a knowledge of only the general thermodynamic properties of the fluid.

Let us imagine a cube in the fluid, which is normally of edge-length λ_0 , distended or compressed into a cube of edge-length λ_1 ; the work done in the process is given by the expression

$$\frac{1}{2} \frac{1}{\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right),$$

where β is the isothermal compressibility of the fluid. Actually as the result of thermal agitation, the cube might change shape as well as volume. If we take the cube to remain always a rectangular parallelepiped, the three edge-lengths may each be either greater or less than λ_0 . It is only one chance in eight that all the edge-lengths would be *greater* (or less as the case may be) than λ_0 . The average work corresponding to a change of one of the edge-lengths from λ_0 to λ_1 may thus be taken to be

$$\frac{1}{16} \frac{1}{\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2$$

and its thermodynamic probability may in accordance with Boltzmann's principle be written as

$$A \exp - \left\{ \frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} d\lambda_1,$$

where A is a constant. If λ_1 be taken to represent a wave-length in the Fourier analysis of the distribution of matter in the fluid, the expression just written is the formula for "the distribution of intensity in the structural spectrum." The expression gives a peak at the wave-length $\lambda_1 = \lambda_0$ with intensity falling off more or less rapidly on either side of the peak. It will be understood that here we are dealing with real periodicities in the distribution of matter, and not merely with fictitious mathematical periodicities as in the discussion of the thermal fluctuations of density. Further, these structural waves pass through the fluid in all directions, and

we may more appropriately write as the expression for the intensity in the structural-spectrum,

$$B \exp - \left\{ \frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} d\lambda_1 d\Omega$$

where B is another constant, and $d\Omega$ is the elementary solid angle.

The problem is now to determine the wave-length λ_0 of the peak in the "structural spectrum." *Prima facie*, we shall not be appreciably in error if we take λ_0 to be identical with the mean distance between neighbouring molecules in the fluid. The evaluation of this mean distance is a very important problem in kinetic theory which does not appear as yet to have been adequately discussed. For an ideal gas, Hertz¹ has shown the mean distance between neighbouring

molecules to be $0.551 n^{-\frac{1}{3}}$ where n is the number of molecules per unit of volume. For a regular cubical arrangement of molecules, λ_0 is evidently equal to $1 n^{-\frac{1}{3}}$, and for the closest²

possible packing $\lambda_0 = 2^{\frac{1}{2}} n^{-\frac{1}{3}} = 1.123 n^{-\frac{1}{3}}$. In a liquid, the arrangement of the molecules is intermediate in type between the absolutely chaotic distribution characteristic of an ideal gas and the regular arrangement characteristic of a crystal. Gans³ has attempted to take into account the finite volume of the molecules in the calculation of the mean molecular distance, and found that with increasing density of the fluid,

λ_0 increases from $0.551 n^{-\frac{1}{3}}$ to $n^{-\frac{1}{3}}$ and even more. His treatment is however open to certain criticisms, and the numerical values given by him cannot be accepted as correct. The problem is considered afresh in a separate paper by one of us, and the general result emerges that for a liquid, λ_0 is

¹ Math. Annalen 67, 387, 1909

² Jean's Dynamical Theory of Gases, 3rd Edition, p. 330.

³ Phys. Zeit., XXIII, 1922, p. 109

$\lambda_n = k^{-1}$ where k is a fraction ranging from about 0.8 to 1.0 according to the nature of the liquid and its condition as to temperature, pressure, etc. λ_0 may also be expressed in terms of the mean linear dimension or diameter σ of the molecule under consideration. The theoretical discussion indicates that in liquids under ordinary conditions λ_0 is of the same order of quantities as σ but may be some 10% to 20% greater.

Liquid Mixtures and Solutions. As we have just seen, the "structural spectrum" of a liquid consisting of only one substance is determined principally by the mean distance between neighbouring molecules and by its compressibility. Passing on to the case of mixtures and solutions, it is not difficult to see that the structural spectrum should, like many other physical characters, be at least roughly an additive property. For, to a first approximation, the volume of a mixture is the sum of the volumes of its components, and hence it is legitimate to assume that the mean distance between two molecules of the same kind in a mixture does not differ notably from what it is in the pure components. Thus if we have a succession of at least three molecules of one kind

A A A

or three molecules of the other kind

B B B

in a line, we have periodicities which are the same as those in the pure components. On the other hand, if we have at least four molecules forming a chain in which the two kinds of molecules alternate,

A B A B

or

B A B A

we would have wave-lengths corresponding to the sum of the two just considered. In the conditions subsisting in a fluid,

the formation of periodic arrays of four or more molecules of this special type is relatively an improbable event, and hence we are justified in assuming that the "structural spectrum" of a mixture or solution would contain principally only those wave-lengths which occur in the pure components. The same reasoning indicates that the distribution of "intensity" in the structural spectrum in the neighbourhood of these principal wave-lengths would be much the same as in the pure components. Hence we may as a first approximation take the structural spectrum of a mixture to be determined by simple addition of the structural spectra of the pure components taken in the proper proportions.

A more exact discussion of the case of mixtures and solutions would involve a consideration of the changes of density and of compressibility which occur when the two substances are mixed, and the influence on the structural spectrum of the local spontaneous fluctuations of density and composition, the precise magnitude of these fluctuations may be determined thermodynamically from the data for the compressibility and partial vapour-pressures of the mixture. *Prima facie*, the local fluctuations of *composition* of the mixture would have very little influence on the structural spectrum. For, we are only concerned with the average effect corresponding to the mean composition of the whole liquid. If the two components make up the structural spectrum in proportion to their respective concentrations, the average effect would be the same as if the liquid was uniform throughout and exhibited no fluctuations of composition. The fluctuations of *density* on the other hand are all-important, as in the case of a pure liquid. The *compressibility* of the mixture therefore enters in a fundamental way in the problem and where this shows marked deviations from the additive rule,¹ the distribution of

¹ For data regarding the compressibility of mixtures and solutions, see Cohen and Schat's *Flexo-Chemie*, Leipzig, 1919, pp. 113-142.

intensity in the structural spectrum would differ from that given by a simple superposition of the spectra of the two components. Any notable change of volume on mixture may also be expected to result in a shift of the positions of the peaks in the spectra

6 *Calculation of the Intensity of X-ray Scattering.*

Having analysed the distribution of matter in the fluid into a "Structural spectrum," in other words, into a number of superposed periodic distributions of different wave-lengths, we proceed to determine the X-ray scattering at different angles by this structure. We ignore the periodicities of larger wave-length which may be identified with sound-waves traversing the medium and which, as we have seen, are only of importance when we discuss the scattering in directions nearly identical with the primary beam. For larger angles of scattering, the periodicities of shorter wave-lengths which arise from the discrete structure of the medium are the only ones that need be considered. It is obvious that each of the periodic distributions of matter into which we have analysed the structure of the fluid would cause an internal reflection or enhanced scattering of the incident X-radiation in the direction given by the Bragg formula

$$2 \lambda_1 \sin \frac{1}{2} \theta = \lambda$$

where λ is the wave-length of the incident X-radiation and λ_1 is the wave-length under consideration in the structural spectrum. Since the structural waves traverse the fluid in all directions, the enhanced scattering or internal reflection corresponding to the wave-length λ_1 would occur in all directions coinciding with the generators of the cone of semi-vertical angle θ . Since λ_0 is the wave-length giving the peak of intensity in the structural spectrum, the special value of θ given by the relation

$$2 \lambda_0' \sin \frac{1}{2} \theta = \lambda$$

gives the cone of greatest intensity of the scattered X-rays, and the scattering would be considerably less both for larger and smaller value of θ . The formation of a fairly well-defined circular diffraction-halo in the X-ray scattering by liquids is thus clearly explained on the conception of the structural spectrum.

From the standpoint of the electromagnetic theory, the problem of determining the effect of the periodic distributions of the matter forming the structural spectrum on the propagation of radiation through the substance is very similar to that solved by Einstein in his paper on light-scattering in fluids except that the law of distribution of intensity in the "Structural spectrum" is different from that in the "Sound-wave spectrum". In fact, we can obtain an expression for the scattering due to the "Structural spectrum" merely by a slight modification of Einstein's treatment for the "Sound-wave spectrum". In the optical problem, we have light-scattering of the same intensity in all azimuths when the incident wave is assumed to have its electrical vector perpendicular to the plane of observation. This is due to the fact that the sound-waves of different wave-lengths which, as explained above, are each separately responsible for the scattering in different directions, are all, in accordance with the equipartition principle, of the *same intensity*. In the "Structural spectrum," on the other hand, the periodic distributions of matter of different wave-lengths follow the special exponential law of intensity

$$A \exp \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1}{\lambda_0} \right)^2 \right\} d\lambda_1$$

(Observing, as before, that each periodic distribution of wave-length λ_1 , is responsible for scattering in a specific direction, the distribution of intensity in the diffraction-halo should obviously follow the law of the structural spectrum very

closely. We may therefore write the intensity of the scattered radiation in any direction θ to be simply

$$C_1 \exp \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^2}{\lambda_0^2} \right)^2 \right\}$$

where λ_1 is given by the Bragg formula

$$\lambda = 2 \lambda_1 \sin \frac{1}{2} \theta$$

and C_1 is a numerical factor.

A useful verification of the formula is obtained by considering the case of a fluid of great compressibility, *e.g.*, a gas. In such a case, β is very large and the formula indicates, as is otherwise to be expected, that the scattering is of equal intensity in all directions perpendicular to the direction of the electric vector in the incident rays. If the incident X-rays are unpolarised, we should multiply the numerical factor C_1 by $(1 + \cos \theta)$ exactly as in the ordinary theory of light-scattering.

The numerical factor C_1 may be evaluated in the following way. In experiments on X-ray scattering, the wavelength λ is generally much smaller than the mean distance between neighbouring molecules. The concentration of the scattered radiation in the form of a diffraction-halo is due to the arrangement of the molecules not being a random one, and hence there existing a correlation of the phases of the waves scattered by neighbouring molecules,—agreement of phase and increased intensity in certain directions, disagreement of phase and diminished intensity in others. The problem is analogous to that of the diffraction of light by a large number of fine holes arranged in a roughly uniform manner in an opaque screen. We know that in such a case, the integrated intensity of the diffracted light in all directions

together is simply equal to the energy transmitted by any one aperture multiplied by the number of apertures. Exactly the same way, c_1 may be found by integrating the energy of the scattered radiation in all directions and putting it equal to the scattering by one molecule multiplied by the number of molecules in the volume under consideration.

7 *Comparison with Observations*

In order to test the indications of the foregoing theory by comparison with experiments on the scattering of monochromatic X-radiation by liquids, we require to know the compressibility β of the liquid and the mean distance λ_0 between neighbouring molecules in the liquid. The latter quantity may be roughly estimated from the known molecular mass M and the density d of the liquid; the best way of finding it is however from the X-ray scattering itself. As is evident, the formula

$$\chi^2 = \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^2}{\lambda_0^2} \right)^2 \right\}$$

when graphed gives a strongly pronounced maximum at the wave-length $\lambda_1 = \lambda_0$, and the general shape of the curve reproduces with striking accuracy, the experimental curves obtained by Hewlett by the ionisation method (See Fig 1C and Fig. 1D above, in comparing which allowance should be made for the imperfect monochromatism of the X-ray pencil used by Hewlett). From the known wave-length of the X-rays used and from the angle of scattering θ_0 for maximum intensity, λ_0 may be found by using the Bragg formula

That λ_0 thus determined is of the same order of quantities

as the value of the mean molecular distance otherwise found is seen from the following table

TABLE.

SUBSTANCE	λ	θ_0	λ_0	$\sqrt{\frac{3}{d}} \bar{M} = n^{-\frac{1}{3}}$	$\lambda_0 \cdot n^{\frac{1}{3}}$
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Results of Hewlett

Benzene	712A	8 5°	4 80A	5 27A	0 911
Octane	„	8 1°	5 04A	6 45A	0 781
Mesitylene	„	6 5°	6 28A	6 13A	1 024

Results of Keesom and Smedt—First paper

Oxygen	1 54A	27°	3 30A	3 59A	0 919
Argon	„	27°	3 30A	3 61A	0 914
Benzene	„	18°	4 92A	5 27A	0 934
Water	„	29°	3 08A	3 09A	0 997
Aethyl alcohol	„	22°	4 04A	4 57A	0 884
Aethyl aether	„	19°	4 67A	5 55A	0 841
Formic acid	„	24°	3 70A	3 96A	0 934

Results of Keesom and Smedt—Second paper

Oxygen	712A	12 5	3 27A	3 59A	0 911
Argon	„	13 0	3 15A	3 61A	0 873
Water	„	13 44	3 04A	3 09A	0 984
Nitrogen	„	11 34	3 60A	3 85A	0 935
Carbon disulphide	„	13 23	3 09A †	4 63A †	0 667

The mean distance λ_0 between neighbouring molecules found from the X-ray data is in every case of the same order of magnitude as $n^{-\frac{1}{3}}$ where n is the number of molecules per unit of volume. The last column gives the value of k where $\lambda_0 = k n^{-\frac{1}{3}}$. It is seen that k is generally about 0.8 or 0.9 as is indicated by theory. It is noteworthy that of the 5 common liquids reported upon by Keesom and Smedt in their first paper, water which has the smallest compressibility has a value of k which is practically unity, while for ether which is highly compressible, k has the relatively low value 0.841.

The compressibilities of the three liquids for which Hewlett has given scattering curves are respectively as follows —

Benzene	90×10^{-11} dyne/cm ²
Octane	120×10^{-11} "
Mesitylene	75×10^{-11} ,

The differences between these are distinctly too small to produce any notable variation in the sharpness of the halo according to the formula. Strictly speaking, however, the halo for octane may be expected to be slightly less sharp than that for benzene or mesitylene. Hewlett's curves seem to indicate that this is actually the case, though owing to the width of the slit used and other complications, the data cannot be regarded as sufficiently precise on the point. Accurate data are as yet not available for any other liquid. It would be of interest to find experimentally whether liquids of high compressibility, *e.g.*, ether, exhibit a more diffuse halo than others, and whether any effect is produced by raising the temperature of the liquid towards the critical point; with rise of temperature and consequently increase of both T and β , the halo may be expected to broaden, and since λ_0 would increase with rise of temperature, the halo should also approach more closely the direction of the primary rays. The scattering at small angles should also increase in accordance with the Einstein-Smoluchowski formula. These indications of theory remain to be tested by observation.

The preceding calculations are based on the analysis of the fine structure of the liquid into a continuous "structural spectrum" having the mean distance λ_0 between neighbouring molecules as its dominant wave-length. While this analysis no doubt correctly represents the facts in broad outline, it leaves out of account the special features arising from the structural peculiarities of the individual molecules and their influence on the distribution of matter in a closely packed assemblage. Other periods, particularly those with wave-lengths much smaller than λ_0 , may conceivably become prominent when a dense aggregation of matter is analysed. In such a case, fainter diffuse haloes may arise outside the principal one. Then again, anomalies may arise in the case of highly asymmetrical molecules in which, instead of a single value of λ_0 , we may have two or even three separate values of the mean distance depending on the special relative configuration of neighbouring molecules. The principal halo would then itself exhibit a complicated structure which might become better defined at lower temperatures when the thermal agitation and its diffusing influence are minimised.

A convenient way of visualizing the complications that may arise in individual cases is to consider the powder diffraction-haloes obtained by the Debye-Scherrer method with the same substance in the solid crystalline state. It is well-known that with the finest powders in which the individual particles are microscopic or ultra-microscopic crystals, the diffraction-rings obtained by this method are relatively diffuse¹. If we imagine the process of subdivision of the individual crystals continued gradually, a stage would be reached when the outer rings would practically all have merged into a diffuse general blackening of the photographic film and even the first few intense rings would have broadened out

¹ See, Szigmondy's *Kolloid-Chemie*, Appendix on the X ray analysis of colloids, by Scherrer

and merged into a single halo. If we imagine all the crystals broken up into individual molecules, we should still get a halo, because, as we have already seen, thermodynamic considerations ensure a certain degree of uniformity in the spacing of the molecules. In view of this analogy, it may be expected that some of the less prominent details of the powder-halo may also survive and find their counterpart in the liquid-halo, though diffused and modified by the expansion or contraction which takes place on melting.

The considerations indicated above suggest that it would be of great interest to compare the diffraction-halo shown in the liquid state with that shown by the same substance in the state of crystalline powder below its melting temperature. Unfortunately, as yet, sufficient experimental material is not to hand for making such a comparison. In two cases, however, that of water and benzene respectively, the necessary data are available. X-ray powder-photographs of ice have been obtained by Dennison¹ and the results have been discussed theoretically by Sir W. H. Bragg,² who has pointed out a defect in the experimental technique of Dennison's work. The spacings observed in A.U. are chiefly, 3.92, 3.67, 3.44, 2.68, 2.26, 2.07, 1.93, 1.92, 1.53, 1.37, 1.30, 1.17. The first four roughly group about a mean 3.42 A.U. and the next four which are nearly coincident give a strong halo at 2.05 A.U. Allowing for the contraction and re-arrangement which takes place on melting, these spacings are in general agreement with the first and second diffraction haloes found for liquid water by Keesom and Smedt. The X-ray powder photograph of solid crystalline benzene taken by Broome³ shows extremely strong haloes corresponding to spacings of 4.90 and 4.16 A.U., a second prominent group of haloes corresponding respectively to spacings of 3.71,

¹ Physical Review, Jan. 1921

² Physical Society's Proceedings 1922, p. 101

³ Phys. Zeits., March 1923, Plate VI

3.44 and 3.11 Å.U. and a third group corresponding to a spacing of about 2.00 Å.U. The first prominent halo of liquid benzene corresponds to a spacing of 4.80 Å.U., while Hewlett's curves also show distinct bumps corresponding to spacings of 3.10 Å.U. and 2.04 Å.U. The agreement appears significant.

Finally, it may be remarked that observations on the X-ray diffraction by liquids consisting of molecules with extended chains of CH_2 groups and the like, *e.g.*, the fatty acids, would be of interest. No data appear to be available regarding these.

Leaving now the case of pure liquids, we may refer in passing to the case of liquid mixtures and of solutions. Wyckoff¹ has studied mixtures of benzene and carbon tetrachloride, water and glycerol, methylene iodide and carbon tetrachloride, and also aqueous solutions of potassium chloride and of alum. The X-ray diffraction-effects shown by the liquid mixtures tried were found by him to be more or less merely superpositions of the effects shown by the components separately. Those due to the aqueous solutions were practically similar to that of pure water. The results for mixtures are in agreement with the approximate theory already indicated. In the case of aqueous solutions, the dissolved material was probably insufficient in quantity to appreciably influence the observed results. Wyckoff has not studied the case of partially miscible liquids. It would be of interest to examine some cases of this kind, special attention being paid to the phenomena observed in the immediate vicinity of the critical solution temperature and for small angles of scattering.

8. *Liquid Crystals.*

Hückel's result, already cited in the introduction, that no notable difference is observable between the diffraction haloes

¹ American Journal of Science, Vol. V, 1923, p. 455

shown by "turbid" and "clear" anisotropic liquids readily receives explanation in the light of the foregoing theory and of the ideas regarding the constitution of these bodies put forward by Oseen in two recent memoirs.¹ Oseen considers separately two types of interaction between the molecules, (a) forces tending to alter the relative positions of their centres of gravity, and (b) couples tending to alter their relative orientation. The equation of state of the fluid is derived by statistical-thermodynamical considerations on the basis of the assumed laws of interaction between the molecules. Both theory and observation indicate that in the turbid anisotropic liquids, there are regions whose dimensions include many wave-lengths of visible light over which the molecules are (at least approximately) similarly oriented. Similarity of orientation does not however necessarily involve any special regularity of spacing² beyond what may be expected on known thermo-dynamical principles from the compressibility of the liquid. It is probable also that the orientations are not exactly identical but that there is only a mean direction about which they oscillate. The absence of rigidity clearly shows that the definite space-lattices characteristic of solid crystals do not exist in the "turbid" fluids. Since the X-ray pattern is determined by the spacing of the molecules, and since what is observed in the experiments is the aggregate effect of groups oriented in all possible directions, it is clear that the diffraction-halo of a turbid

¹ Stockholm Academy, Handlingar, Band 61, No. 16 and Band 63, No. 1, 1921

² In this connection, it is of interest to refer to the experiments of Barker (Jour Chem Soc, 1908, Vol. 80, p. 1120) and Beilby on the influence of a set of regularly arranged molecules on the crystal formation of an isomorphous substance. Barker found that if a thin film of NaNO_3 be allowed to dry on a polished surface of calcite, the crystals of NaNO_3 had their edges parallel to those of calcite. Beilby has shown that even when there are intervening films of foreign material, the orienting influence was exerted through the films provided they were sufficiently thin. Therefore the existence of an orienting influence does not necessarily connote a definiteness of spacing. (Beilby—Aggregation and Flow in Solids, p. 102)

anisotropic liquid would differ little from that of the clear liquid'. The observations of Hückel are thus readily understood.

A detailed comparison of the X-ray photographs for the solid crystalline, anisotropic liquid, and isotropic fluid states for p-azoxyanisole and cholesterylpropionate reproduced with Hückel's paper is instructive. For both substances, the diameter of the liquid halo is approximately the same as that of the most intense group of rings in the crystal-powder photograph. Further, the haloes for the anisotropic and of isotropic liquids state, though very similar, are not absolutely identical and show slight differences in detail. This is not surprising in view of the fact that the compressibility, and other physical properties depending on the molecular arrangement are not identical for the two states. Further studies in regard to this would be well worth undertaking.

The recent studies of Friedel and Royer² and of Friedel³ on anisotropic liquids with equidistant planes are of great interest in this connection. Friedel characterises as the 'smectic' state an arrangement in which the molecules besides having a common direction are in addition arranged in equidistant parallel layers, and which is thus intermediate between the amorphous and crystalline states of matter. To use the phraseology of our present investigation, the "smectic" state is a state of aggregation for which the "structural spectrum" for a particular direction is similar to that of a crystal, but for perpendicular directions is similar to that of a liquid. The X-ray diffraction by the "smectic" state of matter would thus simultaneously exhibit the characters of a crystal and of a liquid in different

¹ The X-ray method of observation is thus in a sense less powerful than the optical one in this particular field. Detailed studies of the scattering of ordinary light by "turbid" anisotropic fluids in different directions and at different temperatures would be of interest in relation to the varying size of the molecular groups.

² *Comptes Rendus, Ser. 1921, June 1922*

³ *Annales de Physique, November, 1922*

directions. The observations of De Broglie and Friedel¹ on the X-ray diffraction by oleate films, and of Piper² and Grindley on the X-ray diffraction by soap-curds may be explained on this basis.

9 *Amorphous Solids.*

It is well-known that many liquids and liquid mixtures when freed from dust may be cooled much below the ordinary melting temperature without crystallization occurring, and that they then pass into a highly viscous or 'glassy condition.' The view has therefore gained general acceptance that vitreous or amorphous solids are really super-cooled liquids, the softening temperature being higher than that of observation. We have already seen that even in liquids, the positions of the molecules are not distributed at random but with a certain degree of regularity depending on the compressibility of the substance. Since, by lowering of temperature, the compressibility of a liquid generally diminishes, it follows that when the substance reaches the highly viscous condition, the molecules are arranged with not less than the degree of regularity characteristic of the ordinary fluid condition. The statement frequently made that in an amorphous solid, the molecules are disposed at "random" is therefore certainly erroneous. It is true we do not have that complete regularity of spacing and orientation characteristic of a crystal. Since an amorphous solid is optically isotropic, it follows that the orientation of the molecules does not lie in any particular direction. But the spacing of the molecules has a considerable degree of regularity. The "structural spectrum" of an amorphous solid is therefore very similar to that of a liquid.

¹ *Comptes Rendus*, March 12, 1918

² *Phys. Soc. of London, Proceedings*, August 1923, p. 269

³ See for instance, G. Tamnmann, "Aggregat Zustand" Leopold Voss, Leipzig, 1922

A valuable confirmation of the views expressed above is furnished by observations on the scattering of light in amorphous solids such as optical glass and in supercooled liquids. Observations with liquids such as salol (phenyl salicylate) which may be converted into glassy solids by sufficiently cooling them show that the light-scattering power in the glassy condition remains of the same order of quantities as in the fluid state. The fact that the optical behaviour of an amorphous solid is very similar to that of a liquid is a justification for inferring that in regard to X-ray diffraction as well, they should behave similarly. The observations of Jauncey by the ionisation method referred to in the introduction, and of Wyckoff (*1C*) show in fact that ordinary glass gives a diffraction-halo very similar to that of a liquid. This does not, as has sometimes been suggested, indicate that glass possesses a rudimentary crystalline structure. The diffraction-halo observed is truly characteristic of the amorphous or non-crystalline condition. The sharpness of the halo is a measure of the regularity in the spacing of the molecules. An extensive series of observations of the X-ray diffraction-halo given by liquids which are supercooled and made to pass into the vitreous condition would be of interest in order further to elucidate the nature of the amorphous condition, and particularly to determine whether, when the temperature is taken below the softening point, any further re-arrangement of the molecules takes place or not.

Incidentally, it may be remarked that the conception of the "structural spectrum" may also be usefully extended to the case of solids and of solid solutions which are not truly amorphous but consist of microscopic or ultra-microscopic crystals packed together. The smaller the crystals, the more diffuse and weaker would be the lines of the "structural spectrum" and the more nearly would the X-ray scattering approximate to that characteristic of a truly amorphous body.

10. *Summary and Conclusion.*

The paper considers the explanation of the diffraction-haloes observed when a pencil of monochromatic X-radiation passes through a film of liquid and is received on a photographic plate. Explanations previously suggested are discussed and are shown to be inadequate.

(1) The explanation of the phenomenon is shown to depend on the consideration that the positions of the molecules in liquids are not at random but possess a certain degree of regularity which can be estimated thermodynamically from the compressibility of the fluid.

(2) The Smoluchowski-Einstein theory of light-scattering in fluids cannot be applied as it stands to the problem of the X-ray scattering owing to the fact that it practically treats the fluid as a continuum, an assumption which is justifiable in the optical case but not in the X-ray problem where the wave-length is much smaller; it is essential here to take into account the discrete structure of the medium.

(3) For very small angles of scattering, however, the Einstein-Smoluchowski theory is applicable even in the X-ray problem, and an explanation is readily forthcoming why liquids scatter very little at such angles.

(4) For larger angles of scattering, the discrete structure of the medium is taken into account by analysing the distribution of matter in the fluid into a continuous "structural spectrum" which has its peak of intensity at a wave-length equal to the mean distance λ_0 between neighbouring molecules. The law of the "structural spectrum" is exponential and is given by

$$A \propto \exp. \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^2}{\lambda_0^2} \right)^2 \right\} d\lambda_1$$

(5) The X-ray scattering in different directions is obtained very simply by combining the law of the structural

spectrum with the Bragg formula,

$$\lambda = 2\lambda_1 \sin \frac{1}{2}\theta$$

and this gives a diffraction-halo with its maximum intensity in the directions for which $\lambda_1 = \lambda_0$. The curve of intensity of the scattering in different directions agrees well with the experimental results of Hewlett, and the mean molecular distance λ_0 with the value deduced from kinetic theory.

(6) A discussion of the case of liquid mixtures indicates that the X-ray diffraction-halo should be practically a simple superposition of the haloes due to the separate components, as has been observed by Wyckoff.

(7) Diffraction by anisotropic liquids is discussed and the experimental results obtained by Hückel, and by De Broglie and Friedel are explained.

(8) Very similar arguments explain the X-ray diffraction-halo shown by amorphous solids

(9) Some of the finer details of the halo observed in the experiments are also discussed and are shown to be intelligible in the light of the theory set out

Annual Report for the year 1922.

1. The Committee of Management beg to submit the following report showing the work done by the Association during the year under review.

2. The Physical Laboratory of the Association continued as usual to be a centre of active research in various branches of the science, and attracted workers from different parts of India and Burma. The following list of papers which were contributed from the Laboratory of the Association or published in its Proceedings during the year 1922 may serve as an indication of the volume of the research work in which the Association has co-operated.

Proceedings of the Association, Vol VII, Pts III & IV.

1. Quetelet's Rings in Mica. By Nihal Karan Sethi, D.Sc, Professor of Physics and C. M. Sogani, M.Sc., Asstt Professor of Physics, Benares Hindu University.
2. On the Colours of Tempered Steel and Other Tarnished Metal Surfaces. By Brojendra Nath Chuckerbutti, D Sc, Asstt. Professor of Physics, Calcutta University
3. Thunderstorms in Trivandrum, By K. R. Ramana-
than, M A., Director, Trivandrum Observatory.
4. An Optical Study of Free and Forced Convection from Thin Heated Wires in Air. By Satish Chandra Pramanik, M.Sc., Research Scholar, Indian Association for the Cultivation of Science
5. On Laminar Diffraction and the Theory of Microscopic Vision By Nalini Kanta Sur, M.Sc., Lecturer in Physics, Ewing Christian College, Allahabad.
6. On the Theory and Some Applications of Sub-synchronous Pendulums. By Durgadas Banerjee, M.Sc,

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Demonstrator of Physics, University College of Science, Calcutta

- 7 On Whispering Galleries By C V Raman, M. A ,
D Sc , Palit Professor of Physics, Calcutta University

Proceedings of the Royal Society, 1922

1. On the Molecular Scattering of Light in Water and the Colour of the Sea By Prof C V Raman.
2. On the Molecular Scattering of Light in Vapours and in Liquids and its Relation to the Opalescence Observed in the Critical State By K. R. Ramanathan, M A

Philosophical Magazine, 1922.

- 1 On the Phenomenon of the Radiant Spectrum By Prof. C V Raman.
- 2 On the Convection of Light in Moving Gases By Prof C V Raman and Dr N K. Sethi.
3. On a New Optical Property of Biaxial Crystals By Prof C V Raman and V S Tamma.

Astrophysical Journal, 1922.

- 1 Einstein's Aberration Experiment By Prof. C V Raman.

Journal of the Calcutta Mathematical Society, 1922

1. On the Disturbed Electron Orbits in an Electromagnetic Field By Panchanon Das, M.Sc.
2. Caustics formed by Diffraction. By P. Das, M.Sc.
3. On the Spectra of Isotopes By P. Das, M.Sc.
4. Ripples of Finite Amplitude on a Viscous Liquid. By J. C. Kameswar Ray, M.Sc.

Nature.

1. Optical Observation of the Thermal Agitation of the Atoms in Crystals By Prof. C V Raman
- 2 Anisotropy of Molecules By C. V. Raman.
- 3 The Colours of Tempered Steel. By Prof C V. Raman.
- 4 Molecular Structure of Amorphous Solids By Prof. C. V Raman.
- 5 The Radiant Spectrum. By C. V Raman
6. Diffraction by Molecular Clusters and the Quantum Structure of Light By C V. Raman.
- 7 Einstein's Aberration Expt. By Prof. C. V. Raman.
- 8 Molecular Aelotropy in Liquids. By Prof. C. V. Raman
9. Opalescence Phenomena in Liquid Mixtures By Prof. C. V Raman
- 10 Transparency of Liquids and the Colour of the Sea. By Prof. C. V. Raman
11. The Spectrum of Neutral Helium. By C. V. Raman

Early in the year under report, your Honorary Secretary accepted an invitation from the University of Madras and delivered a special course of 6 lectures illustrated by experiments on "Recent Developments in Physics" which were attended by crowded audiences from all parts of that Presidency. He also attended the Science Congress at Madras as Honorary General Secretary of that organisation. Later in the year, your Secretary visited the old Government Granary at Bankipur in Patna with a view to study the whispering gallery effect and conducted experiments at the Victoria Memorial and at the General Post Office, Calcutta, with the result that he discovered two new whispering galleries which had remained unsuspected hitherto. Three special lectures were delivered by him at Benares at the invitation of the Vice-Chancellor of the Hindu University during the year

under review. He also visited Vizianagram at the invitation of H. H. The Maharaja to deliver an address to the College Science Association.

Mr. K. R. Ramanathan was deputed by the Madras University with a research scholarship to work at the Laboratory of this Association. He continued his work on the determination of molecular scattering of light in liquids and gases at different temperatures and high pressures up to 100 atmospheres.

Mr. K. Seshagiri Rao was also awarded a special research scholarship by the Madras University to continue his work in our Laboratory on the scattering of light in liquids and gases.

Babu Satish Chandra Pramanik held a research scholarship from the Association during a part of the year under report.

Mr. V. S. Tamma, Professor of Physics, Meerut College, worked here in the Laboratory for about six months on conical refraction in crystals and on the scattering of light in mixtures of phenol and water.

Mr. Lalji Srivastava, Professor of Physics, Government College, Ajmere, worked nearly ten months in the Laboratory on the effect of temperature on the scattering of light in quartz and on the double refraction of rock salt.

Mr. N. C. Krishna Iyer, Professor of Physics, Government College, Rangoon, worked in this Laboratory for nearly three months on the vibrations of strings.

Mr. Nalini Kanta Sur, Lecturer in Physics, Ewing Christian College, Allahabad, worked here for about three months on the scattering of light in smoky quartz.

Mr. D. B. Deodhar, Reader in Physics, Lucknow University, worked here about a month on the scattering of light in gaseous mixtures.

Mr. L. A. Ramdas was working in this Laboratory on the colours of Labradorite and of potassium chlorate crystals.

Mr. S. Bidwai, Lecturer in Physics, Meerut College, worked in this Laboratory for about two months on the colours of haematite crystals

Mr. R. S. Deoras of the College of Science, Nagpur, also worked in this Laboratory for some time.

Mr. S. Ramakrishna Iyer, Assistant Professor of Physics, Maharajah's College, Trivandrum, worked for about 2 months on electrical discharge in gases at low pressures and on the absorption of light in liquids.

Applied Electricity Class

During the latter part of the year under report, Mr. S. K. Dutt, M. A., Dipl. Ing. (Charlottenburg), came forward to deliver a course of lectures on Applied Electricity. We convey our thanks to Mr. Dutt for his taking interest in the Association by delivering such useful lectures. Some 150 students took admission in the above class and about 20 lectures were delivered on the subject.

Department of Chemistry.

During the year under report the general lectures in Chemistry were discontinued as there was no response to the announcement made in the papers and the notices sent to different colleges.

The Commercial Analysis class went on as usual with five students of whom two will appear at the final examination in June 1923.

Mr. R. Venkateswaran of the Burma Educational Service worked at the Laboratory of the Association and contributed an important paper on the 'Molecular Scattering of light in n-pentane' to the Transactions of the Chemical Society of London for December 1922. Prof. Y. Venkataramiah, sometime Vizianagram Scholar of the Association, worked on ultra-violet scattering and absorption in benzene. It is hoped that

the Chemical Laboratory of the Association will soon develop into an active centre of research in Physical Chemistry

Botany Department.

The required number of lectures in Botany for I A. and I Sc. students were delivered by Profs Joytish Chandra Pal and Raj Kumar Sen and the practical classes were held by these professors with the assistance of a demonstrator.

The test examination of the 2nd year Botany class was held in due time The first three students will be awarded prizes. Their names are given in order of merit.—

- 1 Pramatha Nath Dutta.
2. Ramendra Nath Ghosh.
- 3 Harendra Nath Seal

Library.

The following special additions to the Library were made during the year —

1. One set of Annalen der Physik for 20 years.
- 2 One set of Encyklopadie der Mathematischen Wissenschaften.
3. One set of Winkelmann's Handbuch der Physik.
- 4 Kaiser and Runge's Handbuch Der Spektroskopie.

The following publications were also subscribed for as usual.—

1. Scientific American Monthly.
2. Nature.
3. Science Abstracts, A & B
4. American Journal of Science.
5. Philosophical Magazine.
6. Botanical Gazette.
7. Annals of Botany
8. Astrophysical Journal.
9. Chemical News.

- 10 Proceedings of the Royal Society, A & B
11. Transactions of the Royal Society, A & B.
- 12 Physical Review
13. Annalen der Physik.
14. Physikalische Berichte
- 15 Zeitschrift für Physik.
- 16 Physikalische Zeitschrift
- 17 Encyklopadie der Mathematischen Wissenschaften
- 18 Collegian

The Committee have to acknowledge with thanks the presentation of Journals and Periodicals in exchange from the following Societies.—

- 1 The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
- 4 Manchester Literary and Philosophical Society
- 5 American Philosophical Society.
- 6 University of Illinois
7. Faraday Society
8. Franklin Institution
9. American Geographical Society.
10. South African Association for the Advancement of Science
11. Sitzungsberichte of the Prussian Academy of Sciences, Berlin
12. Sitzungsberichte of the Academy of Sciences, Vienna, Austria.
13. University of Pennsylvania, Philadelphia
14. Museum Journal of the University of Philadelphia.
15. Journal de Physique and Radium of the Physical Society of France
16. Publications of the Royal Canadian Institute.
17. Technological and Scientific papers and Circulars of the Bureau of Standards.
18. University of Iowa.

- 19 University of Calcutta
20. Calcutta Mathematical Society
21. Government of India.
- 22 Government of Bengal
- 23 Government of Mysore
24. University of Bombay.
25. Government of Bombay.
26. University of Allahabad
27. University of Punjab
28. Agricultural Research Institute, Pusa.
- 29 Asiatic Society of Bengal.
30. Indian Institute of Science, Bangalore.
- 31 Editor, Indian Engineering

The Committee of Management express their grateful thanks to Rai Chunilal Bose Bahadur, C.I.E., I.S.O., M B, F.C.S., etc, who has kindly expressed his willingness to present the Journal of the Chemical Society, London, to our Association. Several numbers have already been received by the Association

The thanks of the Association are due to the Editors of *the Englishman* and *the Indian Daily News* for gratuitously supplying to the library of the Association their widely circulated daily newspapers and publishing in their columns the daily Meteorological reports of this Institution.

Workshop.

During the year under review a large Universal Cmcinnati-Milling Machine and a 4 H P. motor have been purchased for the equipment of the Workshop. The mechanics turned out the following apparatus during the year —

1. Iron cross tubes for scattering experiments.
- 2 Brass caps to fit the ends of the cross tube, air-tight with glass windows.
- 3 Gunmetal-casting cube for scattering of gas at high pressure.

- 4 Eagle-mounting for 13 ft radius concave grating
- 5 2nd iron cross tubes of 3" diameter with brass nozzles for glass windows
6. One divided circle for fitting up nicol and double image prism.
- 7 One lead-sheet covered box for X-ray tube with slit and windows
8. Four aluminium triangles for chemical work.
- 9 Two rheostats for use with accumulators.
- 10 One iron screw cap with nozzle for piezometer
11. Fitting up one constant deviation spectroscope from different parts purchased
12. Making and fitting a constant deviation drum for the above.
- 13 One conical brass tube for Balopticon projector.
- 14 Fitting up one polarimeter from different parts purchased
- 15 Finishing and fitting up of four pieces of brass screws in iron chairs for adjustable stools
16. Two galvanised iron buckets for garden
- 17 One brass tube for liquid air experiments
18. Making and fitting up of five cross tubes of different angles with zinc nozzles for glass windows for scattering experiments

Purchase of Instruments.

The following instruments were purchased during the year :—

- 1 One big quartz spectrograph.
- 2 One infra-red spectrometer with thermopile and rock-salt prism.
3. One 13 ft radius concave grating
4. One big electromagnet for obtaining fields up to 40,000 Gauss.
5. Three 10" induction coils.

6. Three mercury interrupters, Butt's standard type.
7. One Nutting photometer.
8. One Pulfrich refractometer.
9. One constant deviation spectroscope
10. One Rayleigh refractometer.
11. One polarimeter
12. One pointolite with resistance and extra lamps
13. 2 doz. X-Ray tubes with accessories and rectifiers.
14. One portable resistance with switchboard and ammeter for X-ray coils.
15. One oxygen cylinder with reducing valve and pressure gauge.
16. One CO₂ cylinder with reducing valve and pressure gauge.
17. Microscopical accessories for the Botanical Laboratory

Financial Position.

On the 31st December 1922 the Association had in the custody of the Imperial Bank of India, Government securities of the value of Rs 2,30,400-0-0 for the general fund, Rs 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 3,349-5-6, and cash balance in the office of Rs. 241 4-6, amounting in all to Rs 2,40,490-10-0.

The assets of the Association as shown in its balance sheet on the 31st December, 23, amounted to Rs. 3,83,408-2-4, on account of the general fund and Rs. 68,601-5-0 on account of special funds totalling to Rs 4,52,009-7-4.

On the 31st December 1921 the Association had in custody of Imperial Bank of India, Government securities of the value of Rs. 2,30,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 7,274-5-6, and a cash balance in the office of Rs. 180-14-0,

amounting in all Rs. 2,44,355-3-6. The floating balance in the bank on 31st December 1921 included the special donations of Rs. 3,000 and Rs. 2,000 respectively earmarked for purchase of instruments and equipment, received in 1921 and expended in the following year

The assets of the Association as shown in its balance sheet on the 31st December 1921 amounted to Rs. 3,77,079-1-7 on account of general fund, and Rs. 65,837-14-1 on account of special funds, totalling to Rs. 4,42,917-15-8

The increased assets during the year under report were mainly under the following heads —

	Rs	A.	P.
1. Scientific Instruments	4,314	15	9
2. Botanical Instruments	1,203	1	9
3. Books and Journals for Library	1,815	3	0
4. Addition to Workshop Equipment	4,700	15	9

3½% Government securities for Rs. 2,000 were also purchased for the Association early in December 1922. The transaction however appeared in the Bank's accounts for January 1923, and will therefore be included in the report for 1923.

The thanks of the Association are due to His Highness the Maharaja of Cooch-Bihar, G.C.I.E., etc., for his generous contribution of Rs. 100 per month in aid of the establishment of a permanent professorship and also to the following members who are kind enough to continue their annual subscriptions

1. Raja Peary Mohan Mukerjee, C.S.I., M.A., B.L.
2. Babu Nirmal Chandra Chander, M.A., B.L.

A special donation of Rs. 1,000 was received from the Vizianagram Samsthanam for equipping the laboratory, etc., for which the Committee of Management offers its grateful acknowledgment.

Acknowledgment.

The thanks of the Association are due to their Honorary Engineers Rai Krishna Chandra Banerji, and Babu Bhabadev

Chatterjee, to their Honorary Legal Advisers Babus Jatindra Chandra Bose and Nirmal Chandra Chander, to their Honorary Auditor, Babu Ishan Chandra Bose, to their Honorary Librarian Dr Rasik Lal Datta, to their Honorary Secretary, Prof. C V. Raman, and to their Honorary Assistant Secretaries Babus Jyotish Chandra Pal and Ashutosh Dey for their gratuitous services.

Obituary.

During the year under report the Association has to mourn the loss by death of two of its members who took a lively interest in its cause, Mr E W Vredenburg, who was a member and took an active part in its scientific meetings and Rai Radha Churn Pal Bahadur who was a Trustee and a member of the Committee of Management for the last 16 years

Though not occurring in the year under review the Committee have recorded their deepest sense of sorrow at the great loss they have sustained by the death of our President Raja Peary Mohan Mookerjee Bahadur who was one of our life members, president and a trustee. He took real interest for the welfare of the Association and substantially helped it with a subscription of Rs. 300 per annum. His loss will be severely felt for many years to come. The Association has recorded in a special general meeting its deep debt of gratitude to the revered memory of the late Raja Peary Mohan Mookerjee and a copy of the resolution was sent to his son Kumar Bhupendra Nath Mookerjee to convey their condolence to the bereaved family.

BALANCE SHEET AS ON THE 31st DECEMBER 1922.

Dr.

Balance Sheet as on

	Rs	A	P
To Government Securities $3\frac{1}{2}$ per cent General fund	2,30,400	0	0
" " Ripon Professorship fund	6,000	0	0
" " Nikunja Garabini fund	500	0	0
Value of land and old building	31,680	11	9
Lecture Hall and Gallery	23,465	5	3
Vizianagram Laboratory	40,900	14	0
Range of shops (East side)	2,516	10	9
Range of shops (West side)	2,308	5	0
Darwan's Room	303	13	9
Servants' quarters	1,024	0	0
Observatory	3,116	3	3
Bonus, Provident fund	1,922	0	0
Contribution to Provident fund account	1,803	3	1
Scientific Instrument account General fund	41,640	13	8
" " K K. Tagore fund	25,000	0	0
Botanical Instrument account	2,329	6	0
Library account	23,508	8	4
Tools and Implements account	161	12	3
Workshop Instrument account	9,592	2	3
Sir Richard Temple Prize account	245	0	0
Floating Balance in the Imperial Bank on the 31st December 1922	3,349	5	6
Cash in Office, on the 31st December 1922	241	4	6

4,52,009 7 4

Certified that the accounts for the year 1922 have been audited and found correct.

(Sd) I C BOSE,
Honorary Auditor

the 31st December 1922.

	Rs	A	P.
General fund	3,83,408	2	4
Ripon Professorship fund	10,830	0	0
H H The Maharaja of Cooch-Bihar Professorship fund	21,210	0	0
Hare Professorship fund	1,025	0	0
Victoria Professorship fund	1,000	0	0
Dr Sircar Memorial fund	9,621	0	3
Deposit account	646	14	0
Vizianagram fund account	910	0	0
Provident fund account	2,956	2	1
Medal fund, Woodburn	500	0	0
" " Dr Mahendralal Sircar	3,000	0	0
" " Joykissen Mukerji	9,339	0	0
" " Nikunja Garabini	500	0	0
" " Jatindia Chandia	550	0	0
Interest account Dr M L Sircar Medal fund	420	0	0
" " Ripon Professorship fund	5,718	0	3
" " Nikunja Garabini fund	178	13	2
" " Wood-burn Medal fund	89	0	0
" " Jatindia Chandia Prize fund	77	7	0

4,52,009 7 4

(Sd) C V RAMAN,
Honorary Secretary.

Dr

Receipt and Expenditure during the

	Rs	A	P
To Subscription account	598	0	0
Rent from shops	3,660	0	0
H H The Maharaja of Cooch-Bihar Professorship fund	1,200	0	0
Miscellaneous account	238	11	3
Interest account, General fund	7,909	7	4
„ Ripon Prof fund	190	0	0
„ Nikunja Garabini fund	17	8	0
„ Jatindra Chandra Prize fund	19	4	0
„ Woodburn fund	17	8	0
„ Dr Sircar Research Medal fund	105	0	0
Fees from students	16,192	0	0
Scientific Instrument (Transferred Entry)	3,005	0	0
Bulletins sold account	31	9	0
Provident fund account	707	15	6
Old Material sold account	22	0	0
Dr Sircar Memorial fund	613	0	0
Deposit from students	295	0	0
Vivianagiam fund account	1,000	0	0
Suspense account	739	5	3
Floating Balance in the Imperial Bank on 31st December 1921	7,274	5	6
Cash in Office, on 31st December 1922	180	14	0

44,016 7 10

Certified that the accounts for the year 1922, have been audited and found correct.

(Sd.) I C BOSE,
Honorary Auditor

year ending 31st December 1922.

Cr.

	Rs	A	P.
By Commission account General fund . . .	21	3	0
„ Ripon Prof fund . . .	1	6	0
„ Nikunja Garabini fund . . .	0	3	0
Contribution of Provident fund . . .	220	11	0
Building Repairs account . . .	135	9	6
Cooch-Bihar Prof fund account . . .	600	0	0
Physics Research Scholarship account . . .	550	0	0
Chemistry Research Scholarship account . . .	150	0	0
Scientific Instrument account General fund . . .	5,851	5	9
Municipal Tax account . . .	1,757	6	0
Gas account . . .	582	1	6
Electric account . . .	828	1	6
Provident fund account . . .	250	0	0
Workshop Petty charges account . . .	151	4	0
Postage stamp account . . .	178	12	9
Printing charges . . .	1,342	4	9
Laboratory charges account . . .	3,279	15	9
Library account . . .	2,050	8	0
Furniture account . . .	864	11	0
Electric Installation account . . .	52	8	0
Deposit account . . .	160	0	0
Charges General account . . .	672	10	6
Botany Class account . . .	2,495	0	3
Establishment account . . .	9,023	1	6
Workshop Instrument account . . .	7,764	15	9
Botany Instrument account . . .	1,203	1	9
Miscellaneous account . . .	5	4	7
Suspense account . . .	59	0	0
Vizianagram fund account . . .	60	0	0
Woodburn fund Interest account . . .	105	0	0
Observatory account . . .	9	12	0
Floating Balance in the Imperial Bank on 31st December 1922 . . .	3,349	5	6
Cash in Office on the 31st December 1922 . . .	241	4	6
	44,016	7	10

(Sd) C V RAMAN,
Honorary Secretary.

XI. Electromagnetic Theory of the Scattering of Light in Fluids—Paper B.

BY

K. R. RAMANATHAN, M A., D SC.,

Assistant Lecturer in Physics, University College, Rangoon

■ INTRODUCTION

In a previous paper,¹ the author has worked out a theory of the scattering of light in fluids both for the case when the medium is composed of isotropic molecules and when it is composed of simple anisotropic molecules with random orientation. Since writing the above, there have appeared articles of great interest by Dr. Cabannes^{2,3} and Prof. L. V. King⁴ dealing with the same subject. Some of the arguments and conclusions of these investigators appear to me to be open to question, and in order to clear up the matter, it seems desirable to set forth in somewhat greater detail certain parts of my aforesaid paper. Moreover, it has been pointed out to me by Prof. Raman that there is an error in my investigation of the case of anisotropic molecules which makes it necessary to revise some of the calculations given there. It is proposed in the first part of this paper to discuss the case of anisotropic molecules more fully with the necessary corrections put in and compare the theoretical results with experimental data, and in the second and third parts to review and discuss the theories put forward by Cabannes and King.

¹ Proc Ind Assoc for the Cultivation of Science, Vol VIII, pp 1-22. We shall refer to this paper in the sequel as Paper A.

² Journal de Physique, Ser VI, Tome III, pp 420-442 (1922)

³ Comptes Rendus; Tome 175, p 875

⁴ Nature, May 19, 1923

I. Scattering by a Fluid composed of Anisotropic Molecules

It was shown in Paper A that when a fluid medium of any density is composed of isotropic molecules, the intensity of scattering in any direction is given by the Einstein-Smoluchowski formula when in addition to the external field we take into account the polarisation field due to the neighbouring molecules. If the external field be parallel to O_z and of intensity Z , then the resultant field is also parallel to O_z and is of intensity $Z(K_0+2)/3$, K_0 itself being given by the well-known relation

$$\frac{K_0-1}{K_0+2} = \frac{4\pi}{3} n_0 A$$

Even when the molecules are anisotropic, the resultant field is still given by $Z(K_0+2)/3$ provided the molecules are oriented at random. In this case, however, K_0 is given by

$$\frac{K_0-1}{K_0+2} = \frac{4\pi}{3} n_0 \left(\frac{A+B+C}{3} \right)^2$$

To get the intensity of light scattered in any direction from a unit of volume, we have to add together the contributions from all the molecules contained in it, due regard being paid to the phases of the waves scattered. In the case of isotropic molecules, the induced moments are all parallel to the external field and the direction of vibration in the scattered light is parallel to that in the incident. With anisotropic molecules, however, the directions of the induced moments are fixed in each molecule and the scattered light has in general also vibrations perpendicular to those in the incident light. In a medium composed of anisotropic molecules, the scattering can be supposed to arise out of two causes, one arising from the density fluctuations such as is contemplated in Einstein's theory and the other from the random character of the orientations of the anisotropic molecules.

¹ The notation of Paper A is used.

We may divide the volume of fluid illuminated by the incident light into a large number of equal elementary volumes δv , the linear dimensions of each of which are small compared with the wave-length of light in the medium, but yet so large compared with the size of a molecule that the fluctuations of density in one element may be independent of those in the neighbouring elements. Let us consider one of these elements with its centre at O . In order to get the intensity at any instant of the light scattered from δv , we have to square the algebraical sum of the components of the electric vector from the different molecules, and to get the average intensity over a finite interval of time, we have to calculate the average value of this quantity in a large number of independent trials in each of which the closeness of packing of the molecules and their orientations are re-distributed according to the principles of statistical mechanics. If the incident light be plane-polarised with the electric vector Z parallel to OZ and the direction of propagation be Ox , then at a point P on the y -axis distant r from O , the x -component of the electric vector due to scattering from a molecule at O is given by

$$\frac{p_x^2}{c^2} M_x$$

where

$$M_x = Z \left(\frac{K+2}{3} \right) [\sin \theta \cos \theta \cos \psi (C - A \cos^2 \phi - B \sin^2 \phi) \\ + (A-B) \sin \theta \sin \psi \sin \phi \cos \phi],$$

and θ, ϕ, ψ are the Eulerian angles defining the orientation of the principal axes of the molecule

From all the molecules contained in δv the value is

$$\frac{p_x^2}{c^2} \Sigma M_x$$

Since δv contains a large number of molecules with their orientations at random, ΣM_x would in general be small,

since positive and negative values of M , are equally probable. But it is also possible the values of M , are all positive or all negative, or that the sum of all the positive values is just equal to the sum of all the negative values. These are extreme cases; at any trial, there would in general be a slight excess of the sum of all the positive values over the negative and *vice versa*. Thus, although in a large number of trials, ΣM , would be zero, $(\Sigma M)^2$ would not be. As the late Lord Rayleigh¹ has shown, when the value of M , is as often positive as negative,

$$(\Sigma M)^2 = n \overline{M^2} \delta v$$

where $n \delta v$ is the number of molecules contained in δv . The average expectation of X^2 from δv is thus

$$\begin{aligned} \overline{X^2} &= \frac{p^2}{c^2 r^2} \overline{M^2} n \delta v \\ &= \frac{p^2}{c^2 r^2} Z^2 \left(\frac{k+2}{3} \right) f n \delta v \end{aligned}$$

where $f = \frac{1}{18}(A^2 + B^2 + C^2 - AB - BC - CA)$

When we take the average effect over a finite volume V ,

$$\overline{X^2} = \frac{p^2}{c^2 r^2} Z^2 \left(\frac{k_0+2}{3} \right) f n_0 V \quad (1)$$

The z -component of the electric vector at P in the wave scattered from a molecule at O is²

$$\frac{p^2}{c^2 r^2} M_z = \frac{p^2}{c^2 r^2} Z \left(\frac{k+2}{3} \right) L_z$$

where $L_z = C \cos^2 \theta + B \sin^2 \theta \sin^2 \phi + A \sin^2 \theta \cos^2 \phi$

¹ Theory of Sound, Vol I, p 36

² In paper A, the square of this expression multiplied by $n \delta v$ was taken to represent the intensity of the light scattered from all the molecules contained in δv . This is erroneous, since a part of L_z , namely that arising from the anisotropy of the molecule varies from molecule to molecule

and k is the value appropriate to the density in δv . The value of L_z averaged over all orientations is $(A+B+C)/3$ and the above expression can be written

$$\frac{p^2}{c^2 r^2} Z^2 \left(\frac{k+2}{3} \right) \left[\frac{A+B+C}{3} + \left(L_z - \frac{A+B+C}{3} \right) \right]$$

The square of the z -component of the electric vector from all the molecules contained in δv is therefore

$$\begin{aligned} & \frac{p^2}{c^2 r^2} Z^2 \left(\frac{k+2}{3} \right)^2 \left[\left(\frac{A+B+C}{3} \right)^2 n \delta v \right. \\ & \left. + \left\{ \sum \left(L_z - \frac{A+B+C}{3} \right) \right\}^2 + 2 \left\{ \sum \left(L_z - \frac{A+B+C}{3} \right) \left(\frac{A+B+C}{3} \right) \right\} \right] \end{aligned}$$

The third term is zero when averaged over all orientations. In the second term, $L_z - \frac{A+B+C}{3}$ varies from molecule to molecule and may either be positive or negative, the average value over a large number of molecules with all possible orientations being zero. In such a case

$$\begin{aligned} \left[\sum \left(L_z - \frac{A+B+C}{3} \right) \right]^2 &= n \delta v \left[\overline{L_z^2} + \left(\frac{A+B+C}{3} \right)^2 \right. \\ &\quad \left. - 2 \overline{L_z} \left(\frac{A+B+C}{3} \right) \right] = n \delta v \frac{4}{3} f \end{aligned}$$

because

$$\overline{L_z^2} = \frac{1}{3} (3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA)$$

and

$$\overline{L_z} = (A+B+C)/3$$

The first term varies from one volume element to another owing to the fluctuations of density and the attendant fluctuations of dielectric constant, and as in the case of isotropic molecules (Sec. 3 of paper A), the expectation of the square of the z -component in the light scattered from δv arising out of this cause is

$$\frac{p^2}{c^2 r^2} Z^2 \left(\frac{k_0+2}{3} \right)^2 \left(\frac{A+B+C}{3} \right)^2 \frac{RT\beta}{N} n_0 \delta v$$

The total value of $\overline{Z^2}$ from a volume V is therefore

$$\overline{Z^2} = \frac{p^*}{c^* r^2} Z^2 \left(\frac{k_0 + 2}{3} \right)^2 n_0 V \left[\left(\frac{A+B+C}{3} \right)^2 \gamma + \frac{4}{3} f \right] \quad (2)$$

where

$$\gamma = \frac{RT\beta}{N} n_0 \left(\frac{k_0 + 2}{3} \right)^2$$

The ratio of the weak component to the strong in the light scattered along Oy is

$$Z^2 \gamma \left(\frac{A+B+C}{3} \right)^2 + \frac{4}{3} f$$

When the incident light is unpolarised, the ratio is

$$r = \frac{2f}{\gamma \left(\frac{A+B+C}{3} \right)^2 + \frac{7}{3} f} \quad (3)$$

When the substance is in the form of a vapour so rare as to obey Boyle's law, this becomes

$$\frac{2f}{\left(\frac{A+B+C}{3} \right)^2 + \frac{7}{3} f}$$

Denoting this by r_1 and substituting the values of $\frac{A+B+C}{3}$ and f in terms of the constants of the medium,¹ the above becomes

$$r = \frac{6r_1}{\gamma(6-7r_1) + 7r_1} \quad \text{or} \quad \frac{\gamma}{6-7r} = \frac{r_1}{6-7r_1} \quad (4)$$

The intensity of the transversely scattered light from a volume V at a distance r large compared with the linear dimensions of V is

$$\begin{aligned} & \frac{p^*}{c^* r^2} Z^2 \left(\frac{k_0 + 2}{3} \right)^2 n_0 V \left\{ \left(\frac{A+B+C}{3} \right)^2 \gamma + \frac{13}{3} f \right\} \\ &= \frac{Z^2}{r^2} \left\{ \frac{\pi^2 RT\beta}{9 N \lambda^2} (k_0 - 1)^2 (k_0 + 2)^2 + \frac{\pi^2}{n_0 \lambda^2} (k_0 - 1)^2 \frac{13r_1}{6-7r_1} \right\} V \end{aligned}$$

Substituting r_1 by r and introducing I_0 the intensity of the incident unpolarised light, this becomes

$$\frac{I_0 V}{r^2} \left\{ \frac{\pi^2 RT\beta}{18N\lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left(\frac{6+6_i}{6-7_i} \right) \right\} \quad (5)$$

— the same expression as was first proposed by Prof Raman¹ from general considerations to represent the scattering of light in liquids

In a direction making an angle χ with the incident light, the intensity is easily seen to be

$$\frac{I_0 V}{r^2} \left[\frac{\pi^2 RT\beta}{18N\lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6-6_i}{6-7_i} (1 + \cos^2 \chi) + \frac{12r}{6-7_i} \right\} \right] \quad (6)$$

and the coefficient of extinction becomes

$$\frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6+3_i}{6-7_i} \right\}$$

Comparison with Experiment

Prof. Raman and Mr Seshagiri Rao² have compared the experimental values of the intensity of light transversely scattered by a number of liquids at the ordinary temperature with the values calculated according to (5), and shown that there is satisfactory agreement between the two except in the case of carbon disulphide which shows a very large depolarisation. In table I are included these values and also the values obtained by Messrs Martin³ and Lehrman. To reduce the two sets of values to the same standard, the intensities of scattering for other have been assumed to be the same

¹ "Molecular Diffraction of Light," p 58, and C V Raman and K Seshagiri Rao, *Phil. Mag*, March 1923

² *Phil Mag*, March 1923.

³ *Journ Phys. Chemistry*, Vol. 26, pp 75-88 (1922)

Table I.—Intensity of transversely scattered light in liquids.

The intensities are expressed in terms of that of the polarised scattering of air at N T. P.

Liquid.	Temp °C	$r = \frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent)			Intensity (calculated)	Intensity (observed)	Author
		R & R	M & L	Adopted			
Water	30°	12.5		11.0	159	165	R & R ¹
			6.7			165	M & L ²
Ether	30°	8.3		9.0	930	860	R & R
			10.0			860	M & L (assumed)
Methyl Alcohol	30°	15.1		11.0	512	495	R & R
			7.1			462	M & L
Ethyl Alcohol	30°	13.0		10.0	608	620	R & R
			7.8			485	M & L
n-Propyl alcohol	18°		8.5	8.5	546	630	M & L
Iso-butyl Alcohol	18°		8.5	8.5	610	679	M & L
Iso-amyl Alcohol			9.0	9.0	595	722	M & L
n-Hexane			10	10	835	969	M & L
Cyclo-hexane			8	8	816	750	M & L
Benzene	30°	39.8		48.0	3,000	3,135	R & R
			45.5			2,477	M & L
Toluene	30°	40.0		49.0	4,170	2,970	R & R
			49.0			2,804	M & L
Chloro-benzene			54			3,535	M & L
CS ₂	30°	70		71.0	23,000	16,000	R & R
			71.0			10,850	M & L

¹ R & R, C. V. Raman and K. S. Rao² M. & L. W. H. Martin and S. Lehman.

The last four liquids which have a large depolarisation show a scattering power lower than that calculated

In table II, the polarisation of the transversely scattered light in a number of liquids is calculated from the corresponding values in their vapours according to (4) and the results compared with experiment

Table II

Substance	Weak Component Strong Component (per cent)		
	Vapour	Liquid at 30°C (calculated)	Liquid at 30°C (observed)
Ether .. .	3 0	26 7	9 0
Benzene	6 5	50 4	48
CS ₂	12 0	52	72
CHCl ₃	3 0	26	15
CCl ₄ ..	3 1	37	11

Except in the the case of benzene, the calculated values show no agreement with the observed ones. With carbon disulphide, the observed value is higher than the calculated, while with the others, it is lower. This disagreement between observation and theory seems to show that the molecules in a liquid are not oriented at random. We should, however, still have expected the observed intensities to agree with the calculated, provided we make use of the *observed* values of the imperfection of polarisation. Although there is a good agreement for liquids showing a moderate depolarisation, it is no longer so for liquids showing strong depolarisation. It is remarkable that for these liquids, the observed intensities are *smaller* than the calculated ones.

Dependence of the polarisation of the scattered light on wave-length.

The question whether there is any change in the polarisation of the scattered light when the wave-length is altered is one of considerable interest. Experiments with ordinary gases in the visible region of the spectrum do not show any effect but by reason of their greater depolarisation, liquids may show the effect, which would, however, depend not only on the anisotropy of the molecule, but also on the dispersive power of the substance. Equation (4) shows that even when r_1 remains constant, r would change with the wave-length, the value decreasing with decreasing wave-length, and if r_1 increases with decreasing wave-length (as we might expect it to do for theoretical reasons), the two would act in opposite ways. Previous work in the laboratory of the Indian Association with dust-free carbon disulphide and benzene had failed to show any change of the imperfection of polarisation with wave-length. Cabannes in his recent paper has obtained an effect with carbon disulphide, getting 66 per cent. with red light and 50 per cent. with blue. The experiments have been repeated by the author with the following liquids repeatedly distilled in vacuo, carbon disulphide, benzene, toluene, ethyl ether, ethyl alcohol and water; none of them show a distinct change of r with wave-length. Strong sunlight was used for illuminating the liquids and colour filters for transmitting definite regions of the spectrum—cuprammonium for the blue and Wratten filters for the green and the red. With carbon disulphide, the imperfection was found to be 72 per cent. for white light and practically the same with the different colour filters. At any rate, the values lie between 70 and 75 per cent. The value for benzene was 48 per cent., for toluene 50 per cent. and for ether 9 per cent. In the case of alcohol and water, a difference between the

values has been previously recorded¹ when different colour filters are introduced in the path of the incident light, but a closer examination shows that this is not the effect sought for, but is due to the presence of a trace of fluorescence. This is made quite evident when the colour filters are transferred from the path of the incident beam to that of the scattered. The following tables give the values of the depolarisation

Table III.—Ethyl Alcohol.

	$\frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent)		
	Red	Green	Blue
Filter in incident beam	8.0	7.7	15.0
Filter in scattered beam	11.2	10.2	10.5

The value with no filter was 10.2 per cent

Table IV.—Water.

(Repeatedly distilled in vacuo in pyrex glass bulb.)

	$\frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent)		
	Red	Green	Blue
Filter in incident beam	10.0	10.0	17.5
Filter in scattered beam	10.2	10.8	11.0

¹ C. V. Raman, 'Molecular Diffraction of Light,' p. 55, see also C. V. Raman and K. Seshagiri Rao, Phil. Mag., March, 1923

The value with no filter was 10.8 per cent. The origin of the fluorescence has not yet been definitely ascertained. The alcohol used was the purest obtainable and it was distilled by cooling the condensing bulb with ice, keeping the other bulb slightly above the room temperature. As for the water, a specimen which had already been distilled over alkaline permanganate was used in the distillation bulbs (made of pyrex glass) and the distillations in vacuo were carried out very slowly. In spite of many re-distillations, the effect remained practically undiminished.

II. Cabannes's Theory.

The theory of scattering developed by Cabannes, though in some respects similar to the above, yet differs from it in certain fundamental points. In calculating the effect due to the neighbouring molecules, Cabannes follows the usual method (following Lorentz) of describing a sphere of radius R (small in comparison with the wave-length, but large compared with the linear dimensions of a molecule) about O , and considering the field at O to be made up with two parts, (1) the external field plus the field due to the molecules outside the sphere and (2) the field due to the polarisation of the molecules within the sphere. Lorentz and Rayleigh have shown that for a cubical arrangement of isotropic molecules, (2) is zero. Cabannes considers that although in a sufficiently long time, the components X_1 , Y_1 , Z_1 of this field may cancel, they would at any instant, owing to the irregularities in the distribution of molecules, differ from zero, and the quantities $\overline{X_1^2}$, $\overline{Y_1^2}$, $\overline{Z_1^2}$ would be finite. To calculate these mean values, he takes the mean square of the components $\overline{X_1^2}$, $\overline{Y_1^2}$, $\overline{Z_1^2}$ produced by a single molecule situated in all positions on the surface of a sphere of radius r and in all possible orientations and then sums up the effect for all the molecules contained between two spheres of radii d and R where d is the shortest possible distance between the centres of two neighbouring

molecules. On making the necessary calculations with the implicit assumption that each molecule scatters independently, he arrives at a formula for the imperfection of polarisation of the transversely scattered light from which it appears that even when the molecules of a medium are isotropic, there would be an imperfection of polarisation which would disappear when the density is very small, but which would increase with increasing density. He also obtains a relation between imperfection of polarisation in a liquid and its vapour in terms of the refractivity of the substance and the smallest possible distance between two molecules in the liquid state.

In adding the effects of the different molecules, Cabannes adds the squares of the electric intensities, thus assuming independence of phase between the radiations scattered by the different molecules—an assumption obviously invalid. The calculation of $\overline{X_1^2}$, $\overline{Y_1^2}$, $\overline{Z_1^2}$ also seems to be in error. It is true that in the case of a liquid, when we go down to the individual molecule, the actual field to which it is subject would vary from molecule to molecule, being in part dependent on the positions and orientations of the neighbouring molecules. The residual effect may be looked upon as due to the fluctuations from the cubical arrangement, and the exact magnitude of the fluctuations is not easy to calculate, but the scattering due to this cause may be expected to be small. For, consider a doublet at P with its axis parallel to OX. The electric intensity due to this will diminish as $\frac{1}{r^3}$ so that beyond a distance of a few molecular diameters from P, the intensity will be negligible. The space surrounding the doublet can be divided into two regions such that the x component of the flux of intensity in one is positive while that in the other is negative. These two regions *always accompany each other* and since the volume over which the intensity due to the doublet is sensible is small compared with a wave-length cube, we have to add together the electric intensities

of the scattered waves from the different molecules in this small volume. This sum will be of the second order of small quantities unless there is great asymmetry of distribution round P. The same remarks hold for the y and z components. Cabannes's method of calculation is tantamount to assuming that the positions of the molecules are perfectly random.

In his second paper, Cabannes has adapted Einstein's result to the general case of an isotropic fluid composed of anisotropic molecules by multiplying Einstein's expression for scattering by a factor derived from his own previous investigation. In view of the objections set forth above, this result also cannot be considered as acceptable.

Comparing Cabannes's theoretical results with experiment, it is not true that liquids have always a larger imperfection of polarisation than their vapours at low densities. As the temperature of liquid is raised, the imperfection of polarisation gets smaller and smaller and may reach a value much lower than that for the rare vapour. Experiments on benzene by the author¹ and by Martin and Lehrman² and on carbon dioxide by Raman and the author³ furnish numerous instances of this. In the case of saturated vapour, an increase of density is accompanied by a diminution of the imperfection of polarisation.

Cabannes has deduced the smallest possible distance between the centres of two molecules in a liquid from the depolarizations in the liquid and vapour states. The values obtained are *much too small*. For, example, in benzene, the smallest distance is calculated to be 2.2 Å U, while the average distance⁴ calculated from the density of the liquid on the hypothesis of a close packing of spherical molecules is 7.4 Å U.

¹ Physical Review, 21, p. 564 (1923).

² Journ. Phys. Chemistry, June 1923, pp. 558-564.

³ In course of publication.

⁴ Jeans, Dynamical Theory of Gases.

III. King's Theory.

Prof King's extension of the theory of scattering to media composed of *complex anisotropic* molecules is of considerable interest. With regard to scattering by liquids, he considers that equally probable orientations of complex anisotropic molecules would result in the transversely scattered light being completely polarised. As we have seen in Part I, this is not true. The incompleteness of polarisation of the scattered light cannot, therefore, serve as a basis for the conclusion that liquids have a fine-grained crystalline structure.

In deriving his formula for the intensity of the scattered light in a direction θ with the incident beam, *viz*,

$$\frac{I_{\theta}}{V I} = \frac{1}{2} \frac{\pi^2}{\lambda^4} (\mu^2 - 1)^2 \cdot \frac{6(1+\rho)}{6-7\rho} \frac{RT\alpha}{N} \left\{ 1 + \frac{1-\rho}{1+\rho} \cos^2 \theta \right\},$$

King has apparently neglected to take into account the fluctuations of the polarisation field consequent upon the fluctuations of density. His formula therefore does not reduce to Einstein's in the case when the transversely scattered light is completely polarised. Again, it is not clear why King has used α , the adiabatic compressibility instead of the isothermal compressibility. The compressibility is introduced in finding the work done in changing the actual density at some volume element to the mean density under the condition of ideal thermodynamic equilibrium. Einstein's investigation¹ makes it quite clear that this work must be reckoned isothermally.

Conclusion.

Although the phenomena of molecular scattering do not furnish any definite evidence for the view that liquids possess a crystalline structure, the change of polarisation of a substance from vapour to liquid seems to show that we cannot

¹ Ann der Physik, 33, 1275 (1910), see p 1281.

assume that the molecules have random orientations. As was suggested by Prof. Raman in a letter to *Nature*,¹ there may be temporary groupings of molecules in a liquid having a higher degree of symmetry than the individual molecule. As already mentioned, with many liquids although the calculated values of the imperfection of polarisation are larger than the observed, the calculated intensities agree with the observed values. This can be explained by the assumption of such loose molecular groupings as Prof. Raman has suggested. The presence of these would not appreciably affect the refractivity and so long as their linear dimensions are small compared with a wave length, they would play the same part as the same number of single molecules oriented at random, with the difference that the anisotropic scattering would be altered.

Summary

1 The theory of scattering by a fluid medium composed of anisotropic molecules in random orientation developed in a previous paper is revised and new expressions for the intensity and polarisation of the scattered light and for the coefficient of extinction derived.

With incident light unpolarised, the intensity of scattering in a direction making an angle χ with the incident beam is

$$\frac{I_0 V}{r^2} \left[\frac{\pi^2 RT \beta}{18 N \lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6 - 6r}{6 - 7r} (1 + \cos^2 \chi) + \frac{12r}{6 - 7r} \right\} \right],$$

the polarisation of the transversely scattered light is

$$r = \frac{2f}{\gamma \left(\frac{A+B+C}{3} \right)^2 + \frac{7}{3} f}$$

¹ *Nature*, March 31, 1923. See also Sir W. H. Bragg's note on the above,

and the coefficient of extinction

$$\frac{8\pi^2}{27} \frac{RT\beta}{N\lambda^2} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6 + 3i}{6 - 7i} \right\}$$

2. The theoretical results are compared with experiment. While there is good agreement between the observed and calculated values of the intensity of scattering for liquids having molecules of moderate anisotropy, there is a marked disagreement in the case of liquids with strongly anisotropic molecules

The values of the imperfection of polarisation of liquids calculated from the corresponding vapour values show considerable deviation from the experimental values.

3. A reported change in the imperfection of polarisation of the transversely scattered light in carbon disulphide when the wave-length of the incident light is altered is not confirmed.

Some other liquids have also been examined and the effect has not been found in any of them. Incidentally, it is shown that a change previously observed in the imperfection of polarisation with water and alcohol is due to the presence of a trace of fluorescence.

4. An analysis is made of two recent papers by Cabannes on the theory of molecular scattering of light in fluids and it is shown that the assumption of independence of scattering by different molecules implicitly made therein and his calculation of the effect of local fields are not valid and that his theoretical conclusions are in disagreement with experiment.

5. Some critical remarks are offered about King's theory of scattering in liquids. It is pointed out that his assumption of a crystalline structure in liquids is unnecessary to account for the imperfection of polarisation of the transversely scattered light in liquids. Criticisms are also made regarding his formula for scattering.

The presence of loose molecular groupings having a higher degree of symmetry than the individual molecule would explain the observed low value of the imperfection of polarisation of the scattered light in many liquids.

The experimental observations contained in this paper were made at the Laboratory of the Indian Association for the Cultivation of Science. My warmest thanks are due to Prof C V. Raman for his kind interest in the work and for his valuable advice. The error in my previous investigation was pointed out by him

XII. The Electron Theory of Solids and the Rigidity of Metals.

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1 Introduction.

Sir J J. Thomson in papers published in the Phil. Mag (April and October, 1922) has calculated the bulk modulus of elasticity of a number of metals in the solid state on the basis of the cubical atom model proposed by him, and he finds as the expression for the co-efficient of bulk-modulus (k), for the alkali metals

$$k = \frac{3}{9} \frac{65}{e^2} \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$$

where e is the electronic charge, Δ and M the density and atomic mass of the element respectively. The ideas on which the calculations are made can generally be put in the following words.—

(a) For a monovalent metal the number of electrons per atom is unity. They are distributed at the corners of a cube constructed with the nucleus at the centre; the charges of the nucleus and the electron being E and e respectively, E is equal to e , in order that the atom may be electrically neutral. For di- and trivalent atoms the number of such disposable electrons is respectively twice and three times the number of atoms, and further E being $=2e$ for divalent and $=3e$ for trivalent metals, the solid is kept electrically neutral.

(b) The solid is built up of such cubical cells packed together to fill space and the different atoms and electrons composing the solid are kept in equilibrium by the joint

action of their mutual attractions and repulsions according to laws of force, (i) varying according to the inverse square and (ii) varying according to the inverse cube of the distance

The question of the rigidity of the type of structure postulated by Sir J. J. Thomson arises naturally and does not appear to have been considered so far. In the present paper an expression for the co-efficient of simple rigidity of such atomic structures is obtained for mono-, di-, and tri-valent metals and some of the results so obtained are compared with the experimentally determined values of the co-efficient. It is assumed throughout this paper that the thermal motion of the electrons composing the atoms is *nil*, or in other words, the different atoms and electrons are fixed in their position in space, so that the results obtained take no account of the temperature co-efficient of the constants of rigidity of these elements

The paper also describes special experiments made to determine the modulus of rigidity of the alkali metals sodium and potassium.

2. Method of evaluating the co-efficient of rigidity

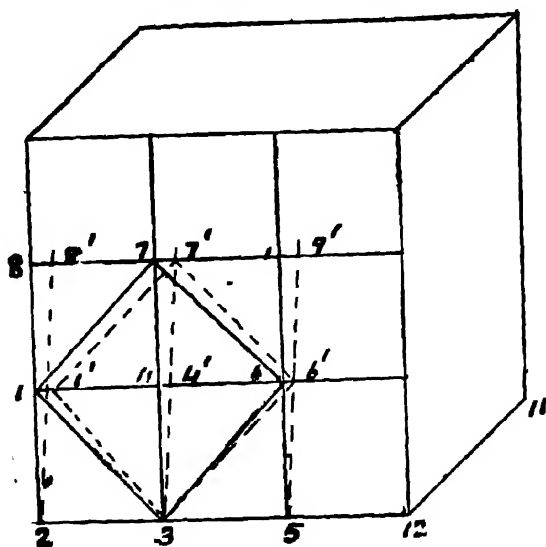


Fig I.

In the classical theory, there are two ways of regarding a shear (i) where the particles of the body are pushed forward by a tangential force as shown in Fig. 1 (the cube 1234 is strained into 1'234'), (ii) the other way is to consider it as an extension in one direction combined with an equal contraction in a direction at right angles to the extension. In the spacial distribution of electrons constituting the atoms of a solid metal, the electrons or nuclei occupy the corners of cubes. Here the two methods of regarding a shear are identical, for what is shear of the former type for the cube 1234, is shear of the latter type for the cube 1367, combined with a rotation of the sheared system through a finite angle. This rotation as a rigid body will not involve any relative motion of the parts of the system and will not call into play any forces depending upon the elasticity of the system. In both these types of shear the work done is stored up as the increase of potential energy of the sheared structure and is equal to $\frac{1}{2}T\theta$ or $\frac{1}{2}n\theta^2$ where T is the tangential stress or pull or push per unit area, n is the co-efficient of rigidity and θ the angle of shear. The increase of potential energy of any electron or nucleus such as 2 (Fig. 1) is obviously the contribution of a series of electrical doublets all directed in the direction of strain and situated at the corners of the undeformed cubes, such as shown in Fig. 1 by 11', 44', 66', etc. The displacements below the datum plane are oppositely directed to those above it. Thus the increase of potential energy for the electron 2 is to be obtained on evaluating $\frac{1}{2}\Sigma\Omega_{..}$ where $\Omega_{..}$ is the potential at 2 of any doublet due to displacement of electron or nucleus at 8. Similarly for a nucleus at 2 the increase of potential energy is to be obtained on evaluating $\frac{1}{2}\Sigma E\Omega_{..}$. Generally the increase of potential energy per unit volume is to be obtained in the form

$$W = k_1\theta^2 + k_2\theta^4 + k_3\theta^6 + \dots$$

where k_1, k_2, k_3 , etc., are functions of e and d (the side of the cube). Since the force is of the two types (i) the inverse

square and (ii) the inverse cube, and act in opposition for equilibrium Ω_1 is of the form

$$\Omega_1 = f \frac{2\mu \cos \phi}{r^3} - \frac{\mu \cos \phi}{r^3}$$

where f as determined from the conditions for equilibrium $= 1.825d$; r is the distance of the doublet 2 from s , μ is the moment of the doublet, $\cos \phi$ is the cosine of the angle of inclination of $2S$ to the plane of the doublet and is expressible in terms of d and θ .

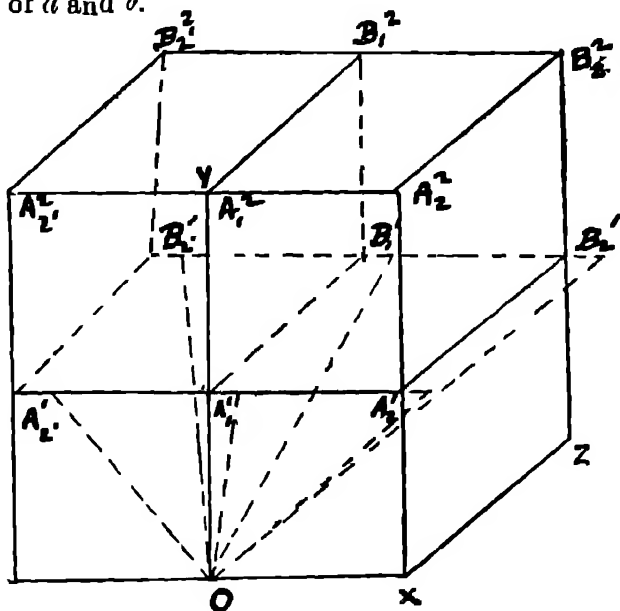


Fig 2

The method of calculation is to take the joint effect of the doublets on both sides of the YZ plane. As nearly equiposed pairs of doublets A'_1 & A'_2 , A''_2 & A''_1 , B_2 & B'_2 , leave a slight positive or negative balance, the calculation for the total contribution for any point O can be made by adding the effects of such pairs of doublets in the different layers and rows. Planes parallel to XYO being called rows, the plane XY is the first of the rows; planes parallel to XYO being called layers, ZYZ' is the first layer.

The contributions for the different layers and rows are given by the following expressions. The doublets nearest the plane OYB—such as A', B', C', etc, being taken singly and the rest in pairs. Only a few expressions are given here, the rest follow easily.

Inverse square law		Inverse cube law	
1st row	A'	$\frac{e^2 x^2}{(d^2 + x^2)^{\frac{3}{2}}}$	$f \frac{e'^2}{(d^2 + x^2)^{\frac{3}{2}}} \times 2$
	A' & A', ez	$\left[\frac{d+x}{\{d^2 + (d+x)^2\}^{\frac{3}{2}}} - \frac{d-x}{\{d^2 + (d-x)^2\}^{\frac{3}{2}}} \right]^{\frac{1}{2}}$	$e' f \left[\frac{d+x}{\{d^2 + (d+x)^2\}^{\frac{3}{2}}} - \frac{d-x}{\{d^2 + (d-x)^2\}^{\frac{3}{2}}} \right] \times 2$
	A' & A', ev	$\left[\frac{2d+x}{\{d^2 + (2d+x)^2\}^{\frac{3}{2}}} - \frac{2d-x}{\{d^2 + (2d-x)^2\}^{\frac{3}{2}}} \right]^{\frac{1}{2}}$	$exf \left[\frac{2d+x}{\{d^2 + (2d+x)^2\}^{\frac{3}{2}}} - \frac{2d-x}{\{d^2 + (2d-x)^2\}^{\frac{3}{2}}} \right] \times 2$
2nd row	B'	$\frac{e^2 x^2}{(2d^2 + x^2)^{\frac{3}{2}}}$	$f \frac{e e^2}{(2d^2 + x^2)^{\frac{3}{2}}}$
1st layer	B' & B', ev	$\left[\frac{d+x}{\{2d^2 + (d+x)^2\}^{\frac{3}{2}}} - \frac{d-x}{\{2d^2 + (d-x)^2\}^{\frac{3}{2}}} \right]^{\frac{1}{2}}$	$ef \left[\frac{d+x}{\{2d^2 + (d+x)^2\}^{\frac{3}{2}}} - \frac{d-x}{\{2d^2 + (d-x)^2\}^{\frac{3}{2}}} \right] \times 2$
1st row	A''	$\frac{4e^2 x^2}{(4d^2 + x^2)^{\frac{3}{2}}}$	$f \frac{4e'^2}{(4d^2 + x^2)^{\frac{3}{2}}} \times 2$
2nd layer	2ex	$\left[\frac{d+2x}{\{4d^2 + (d+2x)^2\}^{\frac{3}{2}}} - \frac{d-2x}{\{4d^2 + (d-2x)^2\}^{\frac{3}{2}}} \right]^{\frac{1}{2}}$	$2exf \left[\frac{d+2x}{\{4d^2 + (d+2x)^2\}^{\frac{3}{2}}} - \frac{d-2x}{\{4d^2 + (d-2x)^2\}^{\frac{3}{2}}} \right] \times 2$

For the electrons and nuclei situated at the centres of the cubes, similar expressions are obtained by putting $\frac{v}{2}$ for x and $\frac{d}{2}$ for d in the expressions such as for $B', B','$, etc. Thus for the nuclei at the centres of the cubes $OA', B', B',$ and $OA', B', B',$ the inverse square law gives

$$-\frac{1}{2}e\epsilon \left[\frac{\frac{d+x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d+x}{2}\right)^2 \right\}^{\frac{3}{2}}} - \frac{\frac{d-x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d-x}{2}\right)^2 \right\}^{\frac{3}{2}}} \right]$$

and the inverse cube law gives

$$-\frac{1}{4}e\epsilon f \left[\frac{\frac{d+x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d+x}{2}\right)^2 \right\}^{\frac{5}{2}}} - \frac{\frac{d-x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d-x}{2}\right)^2 \right\}^{\frac{5}{2}}} \right] \times 2$$

The sign before the last two expressions is to be reversed if the two cubes contain electrons instead of nuclei. Similar expressions hold good for the other pairs in succession. Assuming $\frac{x}{d}$ or θ small enough so that powers higher than the square of θ can be neglected, the above expressions can be simplified and the results are given in the appendix A. The successive figures in the vertical columns indicate the results of pairs taken in order, two every time on both sides of the yz plane. All these results are for the doublets in quarter the whole strained structure, so that from the symmetry of the doublets if we take the moment of those in row 1 as $\frac{1}{4}e\epsilon$ instead of $e\epsilon$, the total increase in the potential energy of an electron or nucleus is twice as shewn by the figures with appropriate signs in the tables, the expression being $\pm \Sigma e\Omega_{2s}$ or $\pm \Sigma E\Omega_{2s}$. In actual summation, as shewn in the

case of the alkali metals below, the contributions are mainly those due to the eight cubes meeting at the point, the rest add a slight correction term and the contributions are therefore taken so as to be correct to the first decimal figure.

3. *Alkali Metals*

For metals of this group, there is one electron for each atom, and further $E = e$. Since all of these metals crystallize in the regular system the nuclei being situated at the centres of the small cubes, the electrons are situated at the corners—one for each corner. As each corner is the meeting place of eight cubes, if we consider the effective electron charge for each cube, at any of the corners to be $e/8$, there being eight such corners for a cube, the total electronic charge is e for each cube which contains the nuclear charge E at its centre. To calculate the increase of potential energy of an electron we find for the eight cubes meeting at 2 (Fig 1),

for the inverse square law

$$\begin{aligned} \frac{1}{2} \Sigma \Omega_{2s} &= 2(+0.500 - 0.177 + 0.351) \frac{\theta^{2,1}}{d} \\ &= 1.351 \frac{\theta^{2,1} e^2}{d} \end{aligned}$$

and for the inverse cube law

$$\begin{aligned} \frac{1}{2} \Sigma \Omega_{2s} &= 4(0.500 + 0.250 - 0.250 - 0.071 + 0.296) \frac{\theta^{3,1}}{d^2} f \\ &= 2.888 \frac{\theta^{3,1} e^2}{d^2} f \end{aligned}$$

A few succeeding terms of the series obtained by adding a layer of one cube every time around these eight cubes are

$$+0.173, +0.085, -0.095, -0.047, \times \frac{\theta^{2,1}}{d}$$

according to the inverse square and

$$-0.023, -0.108, -0.088, +0.017, \times \frac{2\theta^{3,1}}{d^2} f$$

according to the inverse cube law of force.

Correcting, therefore, the increase of potential energy per unit volume of N cubes (each c and E being reduced to $\frac{1}{8}$ th its value for each corner of a cube), as given by

$$\frac{1}{2} N \Sigma c \Omega_{11} + \frac{1}{2} N \Sigma E \Omega_{11} \\ = \frac{1}{64} \left(4 \cdot 18 f \frac{\theta^{1,1}}{d^2} - 3 \cdot 2 \frac{\theta^{1,1}}{d} \right) N$$

The work of a shearing stress per unit volume $= \frac{1}{2} n \theta^2$ where n is the co-efficient of rigidity

Thus we have the equations,

$$\left. \begin{aligned} \frac{1}{2} n \theta^2 &= \frac{1}{64} \left(4 \cdot 18 f \frac{\theta^{1,1}}{d^2} - 3 \cdot 2 \frac{\theta^{1,1}}{d} \right) N \\ N d^3 &= 1 \text{ and } N M = \Delta \end{aligned} \right\} \quad (1)$$

Substituting the value of f and N in (1)

we have,

$$n = \frac{4 \cdot 4 c^2}{32 d^4} = \frac{1}{8} \cdot \frac{1}{M} \left(\frac{\Delta}{M} \right)^2$$

The following table shows the calculated values of n against those observed by the author, as described in the next section

Table I

Metal	Calculated n dynes per sq. cm.	Observed n dynes per sq. cm.
Lithium	0.199×10^{11}	
Sodium	0.218×10^{11}	0.192×10^{11}
Potassium	0.093×10^{11}	0.068×10^{11}
Rubidium	0.075×10^{11}	..
Cæsium	0.053×10^{11}	

1. *Experimental confirmation*

The great difficulty in the determination of the elastic constants of the alkali metals is the vigorous chemical action that takes place when these metals are exposed to the moisture-laden atmosphere, sodium melts away while in the case of potassium the action is attended with fire. Experiments are, therefore, to be made (i) in an inert atmosphere of pure nitrogen or pure hydrogen, or as can be more easily be availed of in an atmosphere of ether-vapour, completely dehydrated by being previously treated with an excess of metallic sodium in a closed vessel, (ii) by dipping the metal in anhydrous kerosene. In both these processes the results are liable to considerable error, by the admission of the slightest amount of the water vapour that may get access to the vessel, owing to formation of a thin crust of hydroxide on the surface of the metal wire. Experiments of a preliminary nature were undertaken avoiding the above difficulties as far as possible, the necessary manipulative skill being acquired by practice.

Sodium being drawn into a wire of 1.1 mm diameter by pressing the metal through the nozzle of the sodium press, was at once transferred to the previously prepared atmosphere of anhydrous ether-vapour in a tall glass cylinder closed by a lid and the wire was subsequently hung from a torsion head and a cylindrical weight of known moment of inertia was fastened at the lower end of the wire. Gentle torsion could be applied by the head being twisted from outside and the period of the resulting oscillation, which lasted only for about a second, was measured by photographic registration of a spot of light reflected from a mirror attached to the inertia cylinder, along with the records of a tuning fork of frequency 60 per sec. Thus it was found that for a sodium wire of length 78 cms and radius 0.677 mms carrying a load of which the calculated moment of inertia was 13.2 units,

the vibration period was 0.25 second. From the approximate formula $n = \frac{8\pi kl}{l^3 r^2 t^2}$ where n , k , l , r , t are the rigidity co-efficient, the moment of inertia of the weight, the length, the radius and the period of vibration of the wire respectively, n is calculated to be 1.92×10^{10} dynes per sq cm. which is closely in agreement with the theoretically calculated value.

For potassium, the procedure adopted in the case of sodium could not be followed on account of its greater chemical activity. Accordingly, a heavy cylindrical weight of mass, about 250 grammes, was hung from a fine wire suspension so that the system when twisted had a period of vibration 7 to 8 seconds. A short piece of potassium wire prepared as in the case of sodium was fixed to the lower end of this cylinder. The other end of the wire was fixed to a massive weight resting at the bottom of a glass vessel filled with kerosene, so that the whole of the potassium wire was merged in the oil. On being gently twisted, and released the system was found to vibrate for a short time with a period of about $\frac{1}{10}$ of a second, which was measured by the optical method of registration as before. The result found for the co-efficient of rigidity of potassium was 6.8×10^9 dynes per sq cm as against the calculated value 9.3×10^9 . The discrepancy in the results both for sodium and potassium is probably to be attributed to the error in the estimation of the mean radius of the wire.

Experiments with other alkali metals have not yet been attempted.

5. *Copper Group*

Although the elements of this group (copper, silver and gold) exhibit varying valency, they are generally considered to be related to the alkali metals in their monovalent character and the regular system in which they all crystallize. But their case stands out different from the structure of

monovalent elements given by Sir J J Thomson Applying the formula for the bulk modulus (k) to these metals the calculated values are much less than the observed values and so are the calculated values of n Table 2 shews the calculated and observed values of k and n for copper, silver and gold. It will be observed that the calculated values are roughly about one-fourth the observed values The difficulty as regards these elements is obviated if the atomic structure is assumed to have twice the electronic charge and twice the nuclear charge instead of one as in the case of the alkali metals. On this assumption, the calculated and observed values shew a better agreement (Table 2, columns 3-4, and 6-7).

Table II

1	2	3	4	5	6	7
Element	k Calculated from Thom- son's formula for the alkali metals	k Calculated on the assumption $E = e = 2e$	k Observed	n Calculated from the formula for the alkali metal	n Calculated on the assumption $E = 2e, e = e$	n Observed
Copper	3.68×10^{11}	14.74×10^{11}	14.3×10^{11}	1.13×10^{11}	1.52×10^{11}	1.55×10^{11}
Silver	2.30×10^{11}	9.21×10^{11}	10.9×10^{11}	0.72×10^{11}	2.88×10^{11}	2.87×10^{11}
Gold	2.41×10^{11}	9.64×10^{11}	16.5×10^{11} 12.5×10^{11}	0.71×10^{11}	2.92×10^{11}	2.77×10^{11}

¹ The latter value is that found by Buchanan (Proc Roy Soc., 1904)

6. Di-valent and Tri-valent metals

Aluminium

A trivalent element when in a solid state must have three electrons for each atom. And if it crystallises in the regular system each atom is to be surrounded by a rhombic dodecahedra of electrons which, when packed together to fill space, are

equivalent to any one of the following space lattice arrangements -

1. Cubical cells—with the nuclei at the corners of the cell¹ and also at the centre of its faces. The electrons are situated at the middle points of the edges of the cell, at the centres of the 8 cubes into which the cell is divided by planes bisecting its edges at right angles. One electron is placed at the centre of the cell. This arrangement gives 4 atoms and 12 electrons per cell.

2. Cubical cells—with nuclei at the middle points of the edges of the cell and one is at the centre of the cell. The electrons are placed at the corners and the centres of the faces and at the centres of the 8 cubes into which the cell is divided by planes bisecting its edges at right angles. This arrangement also gives 4 atoms and 12 electrons per cell.

3. Cubical cells—in which the nuclei are situated at the centres of 4 small cubes, forming the corners of a regular tetrahedron. The electrons are placed at the corners of the large cell, the centres of its edges and at the centres of the small cubes not occupied by the nuclei and one is at the centre of the cell. This arrangement also gives 4 atoms and 12 electrons per cell, of eight small cubes.

In order to calculate the co-efficient of rigidity the increase of potential energy per atom is calculated according to the method used in sections 2 and 3, by putting $E=3e$

Using arrangement (1) the increase of potential energy per electron due to doublets of shear in the eight small cubes is found to be $+6 \cdot 29 \frac{\theta^2 c^2}{d^3} f$ due to the inverse cube law of force and $+1 \cdot 65 \frac{\theta^2 c^2}{d}$ according to the inverse square law

¹ A cell is used to denote a cube with side $2d$ and is composed of 8 small cubes

Using arrangement (2) the corresponding increases of potential energy of a nucleus are $+1.6 \frac{\theta^2 e^2}{d^2} f$ and $-0.186 \frac{\theta^2 e^2}{d^2}$ respectively

Using arrangement (3) the respective increases are $-1.7 \frac{\theta^2 e^2}{d^2} f$ and $-3.56 \frac{\theta^2 e^2}{d^2}$

Since each atom of aluminium is made up of one electron of type (1) one nucleus of type (2) and two electrons of type (3) the total increase is

$$12.79 \frac{\theta^2 e^2}{d^2}$$

Thus, as in Section 3

$$u_{Al} = \frac{12.79}{32} \frac{e^2}{d} N$$

Now $NM = \Delta$ as before and since 4 atoms are contained in a volume $(2d)^3$

$$\frac{1}{d} = 2^{\frac{1}{3}} \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$$

Thus

$$u_{Al} = \frac{12.79}{32} e^2 2^{\frac{1}{3}} \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$$

$$= 2.72 \times 10^{11} \text{ dynes per sq. cm.}$$

$$\Delta_{Al} = 2.70 \quad M_{Al} = 27.1 \times 1.66 \times 10^{-24} \text{ grams}$$

The value of it found from the tables is 2.67×10^{11} , which agrees fairly well with the calculated value.

Calcium.

Of the divalent metals calcium is the one that crystallises in the regular system: the other divalent metals Mn, Zn, Cd, crystallize in the hexagonal system in which the elastic properties vary in different directions. The compressibility of calcium has been calculated by Sir J. J. Thomson using Hull's structure of its crystals and is found to be 5.9×10^{-12} against the experimental value 5.5×10^{-12} .

The crystal of the metal is built up according to the following scheme Cubical cells—having $\frac{1}{8}$ th of a nucleus at each corner and $\frac{1}{2}$ of an atom at the centre of each of its six faces. This makes the total number of nuclei four. The electrons are arranged at the middle point of each side of the cell, one electron at the centre of the cell and one electron each at the centres of the four out of the eight small cubes into which the larger cell is divided by planes bisecting its edges at right angles. These four cubes are chosen so that if one moves parallel to any side of the cell the empty cubes and those containing electrons occur alternately.

Neutral calcium atom consists of one positive nucleus and two electrons—one of the type in which it occurs at the middle point of a side of the cell and the other in which it occurs at the centre of a small cube and for its divalency $E=2e$

The contributions to the increase in the potential energy of the nucleus and the two types of electrons are found to be respectively

$$+2.81 \frac{\theta^2 e^2}{d^2} f, \quad 3.99 \frac{\theta^2 e^2}{d^2} f$$

and 0, for the inverse cube law of force;

$$+0.58 \frac{\theta^2 e^2}{d}, \quad +2.35 \frac{\theta^2 e^2}{d}$$

and 0 for the inverse square law of force.

Thus for the total increase, putting

$$f=1.825d,$$

we get

$$9.47 \frac{e^2}{d}$$

For this metal

$$\frac{1}{d} = \left(\frac{2\Delta}{M} \right)^{\frac{1}{2}}$$

Thus n for calcium

$$= \frac{9.47}{32} \times 2^{\frac{1}{2}} \left(\frac{\Delta}{M} \right)^{\frac{1}{2}}$$

Where

$$\Delta = 1.85$$

$$M = 40 \times 1.64 \times 10^{-24} \text{ grms}$$

The calculated value of n is 7.47×10^{10} . The experimental value for n is not available

7. Summary and Conclusion.

Calculations of the co-efficient of rigidity of the alkali metals have been made on the basis of the atom model proposed by Sir J. J. Thomson (Phil Mag, Vols 43 and 44), and the results obtained have been experimentally verified for sodium and potassium. The calculations include the cases of the apparently complex structures of the metals, copper, silver and gold, which are generally considered to be related to the alkali metals in their monovalent character and the regular system in which they all crystallize. The calculations are extended to the case of the trivalent aluminium and divalent calcium and good agreement is found between the calculated and the observed values for aluminium.

In conclusion, the present writer wishes to accord his best thanks to Prof C V Raman for drawing the writer's attention to the problem and for many valuable criticisms and corrections during the progress of the work

CALCUTTA,

The 3rd September 1923

APPENDIX A.
INVERSE SQUARE LAW.
Electrons.

1st row ¹			2nd row			3rd row		
1st layer	2nd layer	3rd layer	1st layer	2nd layer	3rd layer	1st layer	2nd layer	3rd layer.
$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$
+1 000	+0 250	+0 111	+0 354	+0 178	+0 095	+0 089	+0 088	+0 064
-0 854	+0 143	+0 132	+0 000	+0 136	+0 119	+0 068	+0 049	+0 090
-0 250	-0 088	-0 009	+0 000	-0 049	+0 016	-0 024	+0 000	+0 025
-0 107	-0 092	-0 039	-0 079	-0 071	-0 030	-0 035	-0 033	-0 013
-0 052	-0 062	-0 044	-0 044	-0 089	-0 038	-0 026	-0 034	-0 025

Nuclei

$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$
+0 000	+0 477	+0 252	+0 160	+0 243	+0 173	+0 048	+0 104	+0 076
-0 317	-0 121	+0 044	-0 040	+0 000	+0 050	+0 008	+0 031	+0 046
-0 100	-0 132	-0 050	-0 044	-0 062	-0 023	-0 004	-0 014	+0 000
-0 040	-0 078	-0 058	-0 024	-0 051	-0 033	-0 011	-0 020	-0 048
-0 020	-0 048	-0 080	-0 015	-0 036	-0 045	-0 009	-0 027	-0 022

¹ These figures are to be taken halved in calculation

XIII. On the Fluorescence of Didymium in Glass.

By

N C. KRISHNAIYAR, M.A.,

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Abstract

When white light traverses didymium glass at ordinary temperatures, the track exhibits bright red fluorescence resolved by the spectroscope into four bands, of wave-lengths 475-504, 518-560, 588-612, and 622-645 $\mu\mu$. Some observations on the state of polarisation of the fluorescent light are recorded.

When a pencil of sunlight or light from an electric arc traverses a block of 'didymium glass' (optical glass coloured with didymium oxide), the track is observed to exhibit vivid red fluorescence. A spectroscopic examination of the absorption and the fluorescent spectra with a Hilger constant deviation spectroscope has given the following results. —

Absorption bands observed by Liveing and Dewar in aqueous sols of didymium salts	Absorption bands observed in didymium glass	Fluorescent bands observed in didymium glass
A strong narrow sharply defined band at about wave-length 427 $\mu\mu$	Almost a line at about 430	A band between 475 and 504
A well-marked triplet at about 409, 476 and 488, of which that in the middle is decidedly weaker than the other two	A narrow line at about 472	
	A band between 478 and 483	
A group of two diffused bands with the centre about 510	A band between 509 and 513	
A strong group of about four more or less overlapping bands extending from about 520 to 528	A band between 520 and 530	A band between 548 and 561
A rather weak band at about 531		
A strong group extending from about 570 to 590, consisting of a number of bands overlapping one another	A band between 505 and 598	A band between 568 and 612.
A rather weak band at about 596		
A band at about 670	A band whose more refrangible end is at 678	A band between 622 and 645

The photographs reproduced were taken with a Hilger quartz spectrograph. The wave-length scale not being correctly adjusted, only indicates the region



A is the absorption spectrum of didymium glass about four inches thick when the incident light is from an arc lamp. B is the continuous spectrum of the incident light. C is the fluorescent spectrum when a streak of sunlight traverses the block in a direction parallel to the slit and very near the nearer face of the glass block. The photograph was taken with a narrow slit on Wratten Panchromatic plate, the exposure being twenty hours. This shows the structure of the fluorescent bands lying between the wave-lengths 518 and $645\mu\mu$.

D is the fluorescent spectrum taken with a wider slit. The bands shown in C are here considerably overexposed but the bands in the violet are indicated.

Living and Dewar have investigated the modification of the absorption spectrum of didymium oxide when the freedom of the molecules is diminished in the solid. Comparing the absorption spectra of twenty-five millimetres of fused borax coloured with didymium oxide and that of an equivalent solution of didymium chloride in water, they found that the strong group in the yellow is much expanded and the components of the group unequally shifted towards the red, that the less refrangible of the groups in the green is shifted and its appearance modified, and that the more refrangible bands are much washed out and their shifts very unequal. Similar results are deducible from the

absorption spectrum of the didymium glass. Further, agreement between the absorption spectrum of the didymium glass under experiment and that of Liveing and Newalls' borax tends to show that the didymium in the glass experimented with is of the usual order of purity

The vivid red fluorescent light when examined by Cornu's method did not show any polarised part. But when a piece of cobalt glass was placed between the fluorescent streak and the Wollaston prism, the two images were slightly different in colour (one reddish and the other slightly violet) and about 30% of polarised light could be detected. Seeing that the fluorescent light seen through cobalt glass is faint and that in addition to the fluorescent radiation there is the usual scattering of light in the glass, the scattered light being always partly polarised, further investigation is necessary before any conclusion could be drawn.

The experimental work described in this paper was carried out in the Laboratory of the Indian Association for the Cultivation of Science, Calcutta

XIV. On the Colours of Colloids in relation to the size of the dispersed particles.

By

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The colour and polarisation of light scattered in all directions by particles not very small in comparison with the wave-lengths of light have been studied experimentally by Steubing,¹ Schirman,² Paris,³ Ray,⁴ and others and on the whole their results agree with the mathematical explanation of the action of turbid media on light given by Rayleigh⁵ and Mie⁶ from the point of view of the electromagnetic theory. But the colours of the transmitted light which have an important practical application in the colours of metal glasses, and also the changes of colours of colloidal solutions during coagulation and the axial colours exhibited by clouds of liquid droplets suspended in air as observed by Barus,⁷ have so long been imperfectly understood, and no attempt has been made to bring these phenomena under general theoretical consideration. An attempt will be made in the present paper in the last-named direction.

In order to explain the experimental results of Keen⁸ and Porter, on the transmitted colour of sulphur suspensions, Rayleigh⁹ attempted the solution from energy considerations

Ann der Phys 20, 1908

Ann der Phys 50, 1919

Phil Mag Vol 30, 1915

Proc Ind Ass Vols 7 and 8

Scientific Papers Vols 1 and 4

Ann der Phys 25, 1908 *Koll Zeit*, 1907

Smithsonian contributions 1901, 1907

Proc Roy Soc Vol 80, Ser A, 1914

Proc. Roy Soc Vol 90, Ser. A 1914

The energy of the scattered light which increases rapidly as the size of the particles increases, is derived from the primary beam and hence the energy of the transmitted light decreases *pari passu*, as it passes through the medium with the increase in the proportion of the energy scattered. This only leads to the result that as the particles grow in size, the suspension refuses to transmit first the shorter waves and then finally the whole visible spectrum. Lord Rayleigh did not however find it possible to explain the reappearance of the transmitted light in the later stages, observed by Keen and Porter (*l c*)

Garnett¹ has exhaustively dealt with the colours of metal glasses and of the colloidal solutions of gold and silver. Following Rayleigh, Larmor and others, he first showed that a metal sphere, small compared with the wave-length of light, produces in all surrounding space the same effect as would be produced by a Hertzian doublet placed at its centre. He further showed that, considering a volume which in all its directions is great compared with the wave-length of light and provided the particles are many to a wave-length of light, the suspenoid with its dispersed particles is optically equivalent to a complex medium, whose refractive index and extinction co-efficient depend on those of the particles and of the medium. The colours of the metal glasses and of the metal sols are now explained by Garnett as light absorption by the new complex medium, but the experimental results agree with the theoretical deductions only when the particles are very small, *e g.*, the transmitted colour is red or yellow. It seems that the transmitted blue-violet colours, *ie*, when the particles are larger than in the previous case, cannot be explained on the lines followed by Garnett who suggests in these cases that the particles selectively reflect red and yellow rays and hence the fluid appears blue-violet. But it is extremely doubtful that such a reflection really occurs even when the size

¹ Phil Trans. Ser A, Vols 203 and 205

of the particles is about 100μ . The limitation of this treatment can be seen if the fundamental assumptions are examined more closely. As the particles grow larger, they are not many to a wave-length of light, so that the idea of the complex medium breaks down and we have to examine the light scattering by discrete particles embedded in the medium and distributed in any specified manner.

2 *The Theory of the Colours*

The energy scattered by the particles is derived from the primary beam and hence the intensity of the latter must suffer an attenuation as it passes through the medium. The co-efficient of attenuation is usually derived by a simple calculation of the total energy scattered by an individual particle and then multiplying this by the number of particles per unit volume and then deducting the result from the intensity of the transmitted light. This method is however open to criticism, as it ignores the effects due to the interference of the primary and scattered waves. The more accurate method for the determination of the attenuation co-efficient would be to compound the primary wave with the secondary waves scattered by the particles in the primary direction, with their proper amplitudes and phases. On these considerations, Raman and Ray¹ successfully explained the colours of sulphur suspensions observed by Keen and Porter. It will be seen that the method proposed by Raman and Ray is a general one and applicable to the colours of metal glasses, of hydrosols, and of aero-sols, and other allied phenomena.

The colours of colloids depend on the nature of the particles and of the media, on the shape and size of the particles, and also on their number per unit volume. We shall, for simplicity, assume the shape of the particles to be spherical (as assumed by Garnett, Rayleigh and others) and also that the

¹ Proc Roy Soc Ser A, Vol 100

particles are distributed at random. Consider the passage of a plane wave front through a thin layer of the medium containing n scattering particles per unit volume. We may, following Rayleigh, divide the wave front into elementary areas in accordance with the Fresnel-Huyghens principle, the effect of the secondary waves diverging from these elements at an external point being integrated to find the amplitude and phase of the transmitted wave. In the present case an appreciable part of the area of the wave front is occupied by the scattering particles, which are supposed to be sufficiently numerous and irregularly arranged. We have to consider this part separately from the rest of the wave front. The attenuation of the light in passing through the medium is, according to this procedure, seen to be due to two causes.—

(1) the decrease in the area, and consequently also of the resultant effect of the undisturbed portion of the wave-front; and

(2) the interference with this of the light scattered in the direction of the primary wave by the particles lying in the wave front.

In the case of the very finest particles, the effect contemplated in (1) is very small and the phase of the scattered waves in relation to that of the primary waves is such that the interference effect referred to in (2) does not (to a first approximation) alter the amplitude of the resulting effect, but only affects its phase. With increasing size of the particles, however, the case is altered. The effect (1) becomes considerable and results in a continuous decrease in the transparency of the medium with increasing size of the particles, the number being assumed to be the same. The amplitude of the light scattered by individual particles also increases rapidly at the same time, and the importance of the effect (2) is therefore enhanced; but whether this results

in an increase or decrease of the amplitude of the transmitted wave obviously depends on the phase relationship between the primary and scattered waves in the direction of regular propagation. If the phase of the scattered waves lags sufficiently behind that of the primary waves, we may have actually an increase in the resulting transmission of the light by the suspension with increase in the size of the particles. As we shall see presently, this is what actually happens. Following Raman and Ray (*l. c.*) we are now in a position to write down the expression for the co-efficient of transmission of light through the suspension. Assuming the amplitude of the primary vibration to be unity, the expression for the scattered disturbance due to a single particle in a direction nearly coinciding with $\theta=180$ is

$$\frac{\Lambda\lambda}{2\pi i} \cos \frac{2\pi}{\lambda} (ct - i - \delta)$$

where Λ and δ determine respectively the amplitude and phase. The particles in the stratum are irregularly arranged, but in the direction of the primary wave propagation, the secondary waves diverging from the particles are in agreement of phase and can accordingly combine to build up a plane wave front. The amplitude and phase of this plane wave may be found by integration of the effects of the particles in the stratum in the manner adopted by Rayleigh in his paper on the theory of the light of the sky. Combining the effects due to causes (1) and (2) as discussed before, we have for the effect of passage of the wave through successive strata of the turbid medium

$$E = E_0 e^{-\left(2\pi n^2 x + \frac{\Lambda\lambda^2}{\pi} \sin \frac{2\pi\delta}{\lambda}\right)} \quad (1)$$

where x is the total thickness traversed. (For details of the mathematical steps see Raman and Ray, Proc. Roy. Soc., Ser. A., Vol. 100).

3 *The colours of metal glasses and metal sols*

In order to calculate the amplitude and phase of the secondary waves scattered in the direction of the primary wave, we utilise the formula given by Love as corrected by Rayleigh. In our present calculation we take the substance to be gold particles suspended in water, and we push our calculations for three wave-lengths

$$\lambda = 6300\text{\AA} \text{ U}, \lambda = 5892\text{\AA} \text{ U}, \text{ and } \lambda = 4584\text{\AA} \text{ U}$$

The dielectric constant of the metal is a complex factor and is given by the relation

$$m = n^2(1 - ik)^2$$

where m = dielectric constant of the metal

n = refractive index ,,

k = absorption co-efficient ,,

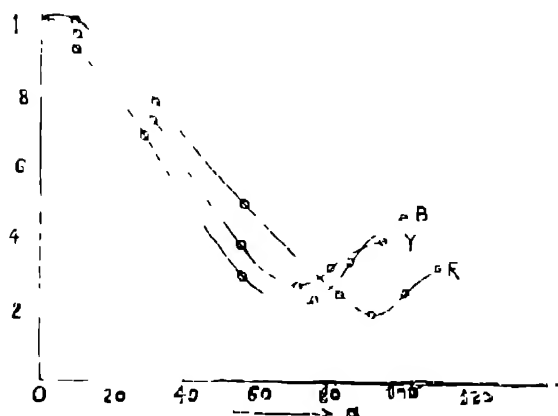
The proper value of the dielectric constant is substituted in the equations and calculations are made in the same way as done by the author previously. The value of n and k are different for different wave-lengths and the actual values are taken from Minor.

λ	n	nk
6300\text{\AA} U	11	3.15
5892\text{\AA} U	17	2.82
4584\text{\AA} U	1.70	1.52

Calculations are made for $ka=1$, $ka=2$, $ka=3$, and by drawing curves, the amplitude and phase of the scattered wave as a function of the ratio $\frac{\text{circumference}}{\text{wave-length}}$ for gold particles in water for each of the wave-lengths $\lambda=6300\text{\AA} \text{ U}$, $\lambda=5892\text{\AA} \text{ U}$ and $\lambda=4584\text{\AA} \text{ U}$ can be obtained.

Since the process of integration considers the effect on the transmitted wave arriving at any given stratum of its passage through all preceding strata, the investigation takes

into account the influence of multiply-scattered light so far as is relevant to our present purpose



The curve I is drawn showing

$$e^{-\left(2\pi\alpha^2 + \frac{4\lambda^2}{\pi} \sin \frac{2\pi\delta}{\lambda}\right)u}$$

as ordinate and α as abscissa. From the graph it will be seen that the colour of the transmitted light is at first red and then it turns to yellow and finally blue. These results are in agreement with observation. In arriving at the equation (1) from the general expressions of Rayleigh (*l. c.*) we have taken that the spherical particles are without any limitations as to their refractive indices and to their radii as well, and we have assumed in these cases that the phases of the scattered waves arising from individual molecules are distributed entirely at random. We have further tacitly assumed that all the particles are of the same size. In the actual experiment, the size of the particles is variable to some extent, but by taking the effective average size, we may obtain a sufficient approximation to the truth; if desired there would be no difficulty in modifying the formula to obtain a more accurate result by

considering separately the effects of particles of different sizes in groups and superposing them to find the resultant.

In this case, the equation is true when the particles are fairly large (contrary to Garnett's assumption) and in the calculation we have considered gold particles in water. We can very easily substitute the value of the refractive index of glass for water in order to find the colours of gold glasses. Also substituting the refractive index of silver for gold in the previous calculation, the transmission colours of silver suspensions in water and also of the silver glasses can be obtained. The curve I gives the general explanation of the observed results.

4. *Colours of aerosols.*

Barus has observed that the colour of the light transmitted through clouds of water, ether, and alcohol drops suspended in air undergoes periodic changes. Taking a typical case, say water, the axial colour is violet-blue when $a = 370 \times 10^{-6}$ cm. With the increase in size of the particles, the colour changes from blue, green, yellow, red, purple, and violet-blue again when $a = 620 \times 10^{-6}$ cm and with still further increase in size, the axial colour changes from green, yellow, red, and violet again when $a = 790 \times 10^{-6}$ cm. No explanation of these periodic changes of colours has yet been given. Recently Werner¹ has repeated this experiment with water drops alone, and measured the intensity of the transmitted light, keeping the number of particles per unit volume fixed, but gradually increasing the size. He has observed that, as the particles increase in size, the intensity gradually decreases till it is minimum and with further increase in the size, the intensity slightly increases but with still further increase in the size, it decreases again.

¹ Ann. der Phys., Vol 70, 1923

In order to explain the colours and also the oscillatory character of the intensity we examine the previous equation

$$I = I_0 \left[1 - \left(2\pi a^2 + \frac{\Lambda \lambda^2}{\pi} \sin \frac{2\pi \delta}{\lambda} \right) n \right]$$

and observe that as a increases both Λ and δ increase, the value of $2\pi a^2$ gradually increases and $\sin \frac{2\pi \delta}{\lambda}$ passes also through maxima and minima, and hence the whole value of

$$\left(2\pi a^2 + \frac{\Lambda \lambda^2}{\pi} \sin \frac{2\pi \delta}{\lambda} \right) n$$

shows an oscillatory character, also since the variation of the value of

$$\frac{\Lambda \lambda^2}{\pi} \sin \frac{2\pi \delta}{\lambda}$$

is small compared with $2\pi a^2$, it follows that the increase in intensity after passing through the first minimum though very small, is appreciable. This explains the general character of the phenomena observed by Barus and Werner. Further we know that $Q = \frac{4}{3}\pi a^3 n$ where Q = water content of the vessel and a the radius of the particles and n the number of particles per unit volume, and if we substitute the value of n in the equation (1), and keep Q constant in the equation, we can express the intensity of the transmitted light in terms of the size of the droplets. The theoretical curves so drawn resemble the experimental values observed by Werner (*loc.*)

Summary and Conclusion

In this paper, (a) the gradual changes of colour of the light transmitted through colloidal solutions, with the increase in the size of the particles, (b) the colours of the metal glasses, (c) the axial colours seen through the droplets of water, ether, alcohol, etc., have been examined. The intensity of the

light in passing through the medium is according to this procedure seen to be due to two causes

(1) The decrease in the area, and consequently also of the resultant effect of the undisturbed portion of the wave front; and

(2) The interference with this light of the light scattered in the direction of the primary wave by the particles lying in the wave front

By combining the resultant effect due to (1) and (2) we get

$$E = E_0 e^{-\left(2\pi a^2 + \frac{A\lambda^2}{\pi} \sin \frac{2\pi\delta}{\lambda}\right) n}$$

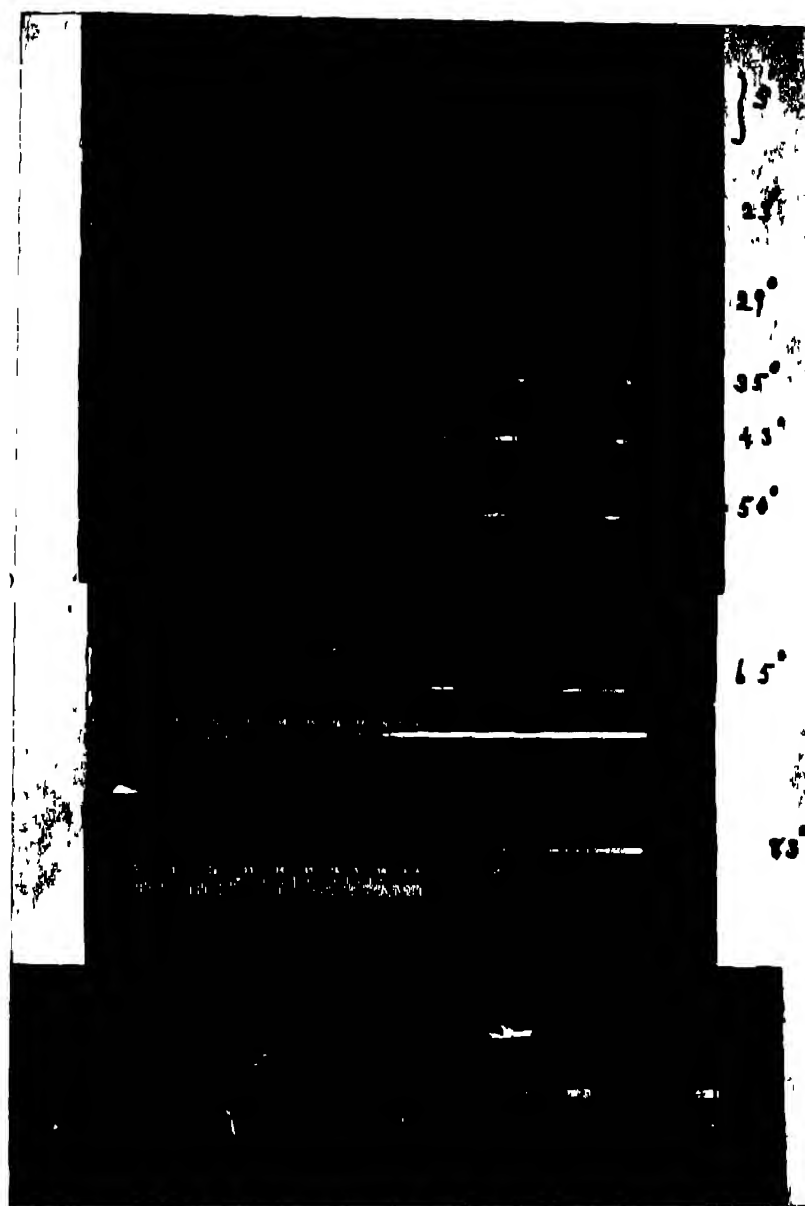
where A and δ are the amplitude and phase of the secondary waves which alter rapidly with the increase in the size of the particles. The second term within the bracket contains a sine factor which becomes alternately a maximum and a minimum when a increases and hence the value of E shows the oscillatory characters observed in the experiment. Since the values of A and δ are functions of λ , the transmitted light becomes coloured.

My thanks are due to Prof C. V. Raman for his interest and helpful suggestions during the progress of the work.

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SPECTRA OF LIGHT REFLECTED BY CHLORATE OF POTASH

XV. Colours of Chlorate of Potash.

By

L A RAMDAS, M.A.,

Palit Research Scholar in the Calcutta University.

(Plate V)

Contents.

- (1) Introduction
- (2) Crystallisation of potassium chlorate
- (3) Measurement of refractive index of potassium chlorate
- (4) Spectrum of the reflected light
- (5) Spectro-photometry of the reflected light and discussion of experimental results
- (6) Conclusion

§ 1. *Introduction.*

The remarkable reflection of light by certain crystals of potassium chlorate was first described by Stokes.¹ The late Lord Rayleigh² worked out a theory of the reflection of light at a twin plane of a crystal. Lord Rayleigh inferred that the reflection is from a large number of twin planes periodically situated. Wood³ experimentally verified this fact by photographing the spectrum of the reflected light in which he got very narrow bands. In the case of one crystal the band was so narrow as to require 700 twin planes.

The presence of these twin planes was actually observed by Dr Hodgkinson⁴ in a specimen mounted in a special way. In this specimen the edges of the twin planes could be seen

¹ P. R. S., Feb., 1885

² Phil. Mag., Vol. XXVI, 1888, pp. 241-265

³ R. W. Wood's Physical Optics, p. 160

⁴ Manchester Proceedings for 1889 Vol. III, p. 117

by means of a hand magnifier. The present Lord Rayleigh¹ has in a recent paper given microphotographs of sections cut at right angles to the twin planes taken with crossed nicols. They clearly show the edges of the twin planes. Similar photographs have also been taken with Madan's crystals where the edges are not equally spaced. This confirms the late Lord Rayleigh's prediction.

In the present paper an attempt has been made to verify the late Lord Rayleigh's theory by spectro-photometry. The refractive index of the crystals has been measured for different wave-lengths for the first time by a simple method, exact calculation being impossible without a knowledge of these values. The conditions under which these crystals are formed have been studied with some care. Spectrum-photographs of the reflected light for different angles of incidence have been taken to study the variation of the width of the maxima with the angle of incidence.

§ 2. *Crystallisation of potassium chlorate*

Pure and dust-free solutions of the salt do not yield any iridescent crystals. A few slightly coloured crystals are sometimes got. They are, however, of the type studied by the present Lord Rayleigh showing complex bands in the spectrum of the reflected light and having only a few twin planes very irregularly situated. They have none of the regularly repeated and innumerable twin planes which exist in the iridescent crystals. In solutions purposely made dirty many coloured crystals are always found. A large quantity of very clean solution was divided amongst five clean vessels. One of them was kept well covered and free from any disturbance. To three other samples small quantities of common salt, potassium chromate and fine dust were added. The remaining sample was attached to a pendulum and given

¹ P. R. S., Vol. 102A, 1923.

regulated shaking. The dusty solution gave a large number of iridescent crystals. The chromate solution also gave a few. The pure solution as well as the one containing common salt gave not even a single coloured crystal. The effect of the shaking was to precipitate the crystallisation. The crystals were formed too quickly to be large but there were innumerable thin crystals of the iridescent type. On the whole a suspended impurity like dust appears to be most effective in forming a large number of regularly arranged twin planes. Foreign matter seems to hinder the continuous and undisturbed growth of a crystal and help the formation of fresh layers which are either actually rotated through two right angles or in which the atoms are arranged in other positions of equilibrium corresponding to those of a crystal rotated through two right angles. The latter appears to be the more probable view.

In this connection it may be interesting to note that Madan's crystals are formed on heating one of the ordinary crystals to nearly its fusing point, when the amplitude of the atomic vibrations has nearly reached the maximum value which it can attain without breaking down the crystal structure, and then allowing it to cool. After the atoms have gained sufficient energy for them to assume alternative positions of equilibrium corresponding to those of a crystal turned through two right angles, they slowly come to rest on cooling and show the twinned structure which has been studied by both the late and the present Lord Rayleigh. The former has shown that the effect of heating is not to form actual cavities inside the crystal but to form twin planes as in the iridescent crystals. Spectrum-photographs of the reflected light and microphotographs of sections of Madan's crystals have been taken by the latter which show that the twinned structure is complex. It appears that twin crystals of Leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$), on heating, lose all traces of the twin planes which they had before, and are

converted into ordinary crystals on cooling. It would be interesting to study the structure of ordinary as well as indescent crystals of potassium chlorate with the help of X-rays. No less interesting would be the study of the changes in the Laue patterns of an ordinary crystal on heating to nearly 250° and then allowing it to cool

§ 3 *Refractive index of potassium chlorate.*

It was found that no data are available for the refractive indices of the crystal for different wave-lengths. They were determined by the following simple method.¹

A fairly big-sized and thick crystal was attached to a pin with one of the edges vertical and it was immersed in a small quantity of carbon-disulphide contained in a cell with parallel glass windows. An illuminated slit was viewed through the cell keeping the edge of the crystal in a line with the eye and the slit and parallel to the latter. On turning the crystal about a vertical axis a position was found for which a well-defined spectrum was formed far away on one side of the slit. On carefully observing this spectrum it was found to consist of two spectra slightly separated from each other and polarised at right angles (vertically and horizontally). The spectrum nearer the slit was polarised with vibrations vertical.

The spectra had the red towards the slit. By adding benzol in suitable quantities the refractive indices for different colours were made equal both in the liquid mixture and in the crystal, beginning with the red. At each stage the particular colour for which the indices are equal coincides with the slit. The measurements were made only for the nearer spectrum. The refractive indices of the liquid

¹ "On Wave-propagation in Optically Heterogeneous Media and the Phenomena observed in Christiansen's Experiments" By Dr Nihal Karan Sethi (Proc Indian Association, Vol VI, p 121)

mixtures were measured with the help of a Pulfrich Refractometer calibrated each time for the particular colour under consideration with the help of pure benzene and toluol whose refractive indices are known for different regions of the spectrum. For yellow light the sodium flame and for the other colours the light from a candle flame were used. The refractive index-wave-length graph was drawn so that the refractive index may be roughly ascertained for any wave-length. From two known values of the refractive indices for two wave-lengths Cauchy's constants were calculated so as to check the values obtained for other wave-lengths.

Table I.

Refractive index of KClO_4

COLOUR	$\lambda \times 10^8$	μ (experimental)	μ (calculated)
Red	6500	1.529	
Yellow	5896	1.531	
Green	5000	1.539	1.537
Blue	4500	1.544	1.541
Violet	4000	1.549	1.547

$$\mu = A + \frac{B}{\lambda^2} \quad \begin{aligned} A &= 1.518 \\ B &= 4.7 \times 10^{-11} \end{aligned}$$

§ 4. *Spectrum of the reflected light*

The coloured crystals were carefully selected from each crop, washed with a small quantity of distilled water, dried on filter paper and transferred to a card-board box. The light reflected from one of these crystals was found to be extremely interesting. There were two, and in some positions, three orders of maxima in the visible region of the spectrum, each maximum with secondary maxima (three in some cases) on either side. The repetition of the same structure in the various orders of maxima is the best evidence for the identity of their origin. The presence of the secondary maxima is exactly in accordance with the explanation put forward by

the late Lord Rayleigh The present Lord Rayleigh has observed similar secondary maxima in the spectrum of the light reflected by "Pelidnota Sumptuosa"

The accompanying plate (Plate V, fig 1) was taken with the bigger type quartz spectrograph of Adam Hilger (using panchromatic plates) It is very interesting to note how enormously the widths of the maxima decrease as they are made to travel from the violet towards the red end of the spectrum by decreasing the angle of incidence Against each spectrum is marked the angle of incidence Plate V, fig. 2, is a photograph of the spectrum taken with the carbon arc and it shows five orders in the blue, violet and ultra-violet (4th, 5th, 6th, 7th and 8th orders respectively) The positions of the maxima are marked The photograph was taken with an ordinary plate and so the 3rd order in the red has not come out.

The co-efficient of reflection of a twin plane is zero at normal incidence and increases rapidly as the angle of incidence is increased, so that the effective number of twin planes reflecting (once the reflection has become total at about 15° angle of incidence) decreases rapidly in proportion This readily accounts for the change in the width of the lines for different angles of incidence. With the aid of a travelling microscope the widths of the various orders of maxima as well as their wave-lengths were measured. It is evident that $\frac{\lambda}{n\lambda} = n \times m$, where n is the order of a band and m , the number of twin planes acting. In the present case it is justifiable to assume that each plane reflects only once as the distance t between two consecutive planes multiplied by m when the incidence is nearly normal (*i.e.*, when all the planes are contributing to the reflected light) is very nearly equal to the total thickness of the crystal.

$$m \times t = 35 \times 0.00664 = 0.23mm \text{ (} t \text{ being calculated for a yellow band)}$$

$$m \times t = 35 \times 0.00670 = 0.235mm \text{ (} t \text{ being calculated for a blue band)}$$

The actual thickness measured by means of a microscope was about 0.25mm n was calculated from the positions of the successive orders in one of the spectra, the refractive indices of the corresponding wave-lengths being known already. In the formula $2\mu t \cos i = n\lambda$, i , the actual angle of incidence at the twin plane (r is the angle of refraction into the crystal) is different for different colours and t is calculated from a knowledge of μ , the refractive index, and the angle of incidence at the external face of the crystal. The value of n was found to be 3, the three orders visible in most of the spectra in the plate being the 3rd, 4th, and 5th respectively. m , the number of planes acting was thus calculated for the wave-lengths corresponding to the three maxima in the spectra photographed

The late Lord Rayleigh derived the following expression for the amplitude of the light reflected from a single twin plane —

$$\eta = \frac{B}{2D} \frac{\sin \phi}{\cos^2 \phi}$$

where η is the co-efficient of reflection, B , D the dielectric constants of the crystal and ϕ is the angle of incidence at the twin plane. For the aggregate reflection from a series of twin planes (m in number) ¹

$$\phi m^2 = \tan h^2 m \beta_1$$

where

$$\beta_1 = \pm \tan h^{-1} \eta$$

or

$$\eta = \tan h \frac{\beta_1}{2}$$

when the light is totally reflected, $\tan h^2 m \beta_1 = 1$

But

$$\eta = \frac{B}{2D} \frac{\sin \phi}{\cos^2 \phi} = \tan h \frac{\beta_1}{2}$$

Knowing

η and ϕ , $\frac{B}{2D}$ can be estimated

The values are given in Table II.

¹ Proc Royal Society, No A-050, Oct 1917, 'On the Reflection of light from a Regularly Stratified Medium'

Table II.

Measurement of the widths of the bands in the photographs, and the calculation of the number of plates reflecting and η are given below.—

θ = angle of incidence at the external face of the crystal

ϕ = actual angle of incidence at twin plane = angle of refractor given by $\sin \phi = \frac{\sin \theta}{\mu}$

θ	n	$\lambda \times 10^{-4}$	$d\lambda$	λ $d\lambda$	m	$m\beta_1$	β_1 z	$\eta = \tan h \frac{\beta_1}{2}$	$\frac{\sin \phi}{\cos \phi}$	$B = \frac{\eta}{2D \sin \phi \cos^2 \phi}$
50°30'	3	5850	119.4	49	16		156.3	1541	6748	2284
	4	4500	112.7	40	10		2500	2451	6670	3676
	5	3670	95.08	38.63	8		3125	3028	6606	4583
43°20'	3	6125	123.9	49.4	17		1471	1464	5610	2610
	4	4600	97.53	47	12	5	2084	2069	5547	3731
	5	3771	74	51	10		2500	2450	5507	4449
35°30'	3	6150	118.9	51.99	18		1389	1381	4474	3116
	4	4730	83.62	56.57	14	5	1785	1765	4392	4019
	5	3850	53.48	72.01	14		1785	1765	4243	4160
29°20'	3	6220	109	57.1	19		1316	1309	3768	3664
	4	4810	67.45	71.3	18	6	1389	1381	3540	3802
	5	3950	46.10	85.1	17		1471	1464	3518	4182
23°	3	6250	91.56	68	23		1086	1081	2782	3860
	4	4850	68.34	71	18	5	1389	1381	2713	5091
	5	3980	44.36	90	18		1389	1381	2686	5121
4°	3	4900	33.34	150	37	5	0876	0676	0454	1.485
	4	4460	26.35	156	31		0833	0.90	0452	1.836

§ 5. *Spectro-Photometry.*

The photometric measurements were made by means of Hulger's Nutting Spectro-Photometer in series with an ordinary spectroscope fitted with an adjustable slit in the focal plane of the eye-piece. The adjustable nicol of the photometer was set for complete extinction of the central spectrum, the reading in the graduated circle being then 0° . Thus if the reading is θ when the spectrum is adjusted to be equal to the two spectra given by some other source, $\sin^2 \theta$ gives the ratio of the intensities of the two sources compared. In a line with the aperture which gives two images a small spectrometer was adjusted so that the reflected light coming from the crystal mounted vertically on the prism table passes through the telescope deprived of its lens and eye-piece. The use of this additional spectrometer for the crystal is only to enable accurate measurement of the angle of incidence at the crystal face. The two sources were always kept at the same distance from the two apertures of the Nutting photometer. The ratio of the two sources was measured for different regions of the spectrum before calculating the correct reflecting power of the crystal. The two sources were a half-watt lamp and a 50 candle power electric bulb.

It is evident from Table II that for a given angle of incidence at the external surface of the crystal the value of η increases as the wave-length of the reflected light decreases; but in calculating $\frac{\sin \phi}{\sin^2 \phi}$ we assume that B varies for different wave-lengths as indicated by the values of $\frac{B}{2D}$ in the last column and that the reflection co-efficient η varies exactly as $\frac{\sin \phi}{\cos^2 \phi}$. It has to be borne in mind that the theory of Lord Rayleigh is not concerned with dispersion, but assumes that only light of a particular wave-length is

zero to about 30° slowly it was found that the black band in the blue became completely black for a smaller angle of incidence than the minimum in the red. This is in agreement with the higher value of η for the shorter wave-length

Spectro-Photometric Measurements

Table III gives the variation of the intensity of the reflected light on rotating the crystal in its own plane, keeping the angle of incidence constant. Lord Rayleigh has remarked that it should vary as $\sin^2 \theta$ where θ is the angle between the plane of incidence and the plane of symmetry of the crystal $\frac{\sin^2 \theta}{\sin^2 \phi}$ ought to be constant which it fairly is for large values of θ (say greater than 30°) The experimental difficulties are greater for smaller values of θ

Table III.

ϕ = reading of photometer

θ	ϕ	$\sin \theta$	$\sin^2 \phi$	$\frac{\sin^2 \phi^1}{[\text{for twin plane}]}$ alone	$\frac{\sin^2 \theta}{\sin^2 \phi^1}$
0	$9^\circ 45'$	0	0.287	0	
10°	$10^\circ 15'$	0.301	0.317	0.3030	10.04
20°	$13^\circ 30'$	1.169	0.545	0.258	4.53
30°	$23^\circ 30'$	2.500	1.590	1.301	1.92
40°	83°	4.130	2.966	2.679	1.54
50°	$40^\circ 15'$	5.866	4.175	3.888	1.51
60°	48°	7.499	5.524	5.237	1.43
70°	57°	8.831	7.034	6.747	1.31
80°	$64^\circ 33'$	9.701	8.147	7.860	1.23
90°	$70^\circ 30'$	1.0000	8.888	8.601	1.16

$$\sin^2 \phi^1 = \sin^2 \phi - \sin^2 \phi (\theta=0)$$

where $\sin^2 \phi (\theta=0)$ = the reflection from the external surfaces alone,

For angles of incidence up to 30° there was no difficulty of adjustment. For smaller angles a mirror had to be used for reflecting the light to get the required angle of incidence. Corrections have been made for the light reflected by the external surface.

Table IV.

Intensity for different values of the angle of incidence

θ	Red	Orange	Yellow	Green	Blue	Indigo	Violet
$66^\circ 15'$			07947				1389
65°			06695				1447
$61^\circ 45'$			09521				1206
54°			1041				1346
45°	1297					2513	
$42^\circ 15'$	0893				1667		
$34^\circ 30'$	0425				0974		
$29^\circ 15'$	0414				0588		
$25^\circ 21'$					0693		
$21^\circ 15'$				0779			0888
$16^\circ 45'$				0681			
7°				0070			
5°				0021			

The above values are not absolute. They are only for comparison. The fractions in the Table are the ratio of the intensity of the reflection by the crystal to that of the comparison source.

§ 6. Conclusion and Summary.

From the measurements given in Tables II and IV it is clear that interference effects prevent the measurement of γ for

all angles of incidence for a definite wave-length. It is necessary to secure a crystal which is known for certain to have only a single twin-plane, in order to verify Lord Rayleigh's theory.

(1) In the present paper the cause of the formation of the iridescent crystals is experimentally found to be the presence of dust and other suspended or dissolved impurity.

(2) The variation in the reflection co-efficient with the angle of incidence has been calculated and also spectrophotometrically measured and it has been found that η varies with λ , being more for shorter wave-lengths.

(3) The variation of the intensity of reflected light when the crystal is turned in its own plane without altering the angle of incidence has also been measured experimentally.

(4) The refractive index of the crystal has been measured for different wave-lengths.

(5) Photographs of the spectrum of the reflected light have been taken showing clearly the presence of secondary maxima on either side of the central band, sometimes three in number and also showing the change in the width of the central maxima of the various orders as the angle of incidence is changed. It is found that with increasing angle of incidence the number of twin-planes which contribute appreciably to the observed effect rapidly diminishes.

In conclusion, I wish to state that the above work was carried on at the Indian Association for the Cultivation of Science while the author was in receipt of a research scholarship from that institution and that my best thanks are due to Prof. C. V. Raman, M.A., D.Sc., for his valuable help and advice.

XVI. On the Colours of Mixed Plates.

Part IV

By

K SESHAGIRI RAO

In the third paper of this series¹ the consequences of the new theory advanced in the second paper to explain the phenomena shown by mixed plates had been worked out in detail and the results obtained have been shown to be in agreement with experiment. In this paper it is proposed to deal with some further studies of the phenomena including those of dry films

Intensity Distribution in the Halo.

The detailed description of the phenomena has been given in the first paper. The remarkable feature of the phenomena is that though the bubbles vary in size and shape arbitrarily and are irregularly arranged in the film, the diffraction halo exhibits a regular structure consisting of a series of circular rings which are close together in the centre of the halo and wider apart in the margin, the number of rings depending only on the thickness of the film and its composition. The theory proposed is that these effects are due to the scattering of light from the laminar diffracting edges in the film. Owing to the action of surface tension, the edges are drawn inwards as a meniscus which in this particular case may be assumed to be semi-circular. The theory worked out on this basis shows that the scattered light consists of two

¹ Phil Mag., March 1921, June 1921 and September 1921

sets of dark and bright circular rings, the first set extending to large angles of diffraction and the second of inappreciable intensity except at the centre of the halo.

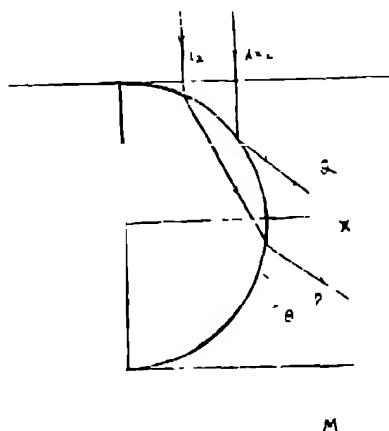


Fig 1

The first is due to the interference of pencils P, Q and the other to the diffracted pencils L and M. The two sets of rings would be superposed on each other at the centre giving rise to the composite character of the halo. The position of dark rings in the first set is given by the angle of diffraction θ where

$$\{1 - \mu \sin i\} \{ \mu \cos i - \sqrt{1 - \mu^2 \sin^2 i} \} - \delta = \lambda \quad (1)$$

$$\mu \sin i = \sin r \text{ and } \sin \theta = \mu \sin 2(i - r)$$

δ = phase change occurring in total reflection depending upon the plane of polarisation of incident light.

The second set are determined by

$$(\mu - 1)t + \frac{t}{2} \sin \theta - \frac{\lambda}{2} = (2n + 1) \frac{\lambda}{2} \quad \dots (2)$$

We shall now consider the relative intensity of the interfering pencils. The experimental observations already recorded show the interferences to be remarkably perfect and hence the interfering pencils must be of comparable intensity throughout the region in which we have maxima and minima.

That is what should be expected from considerations advanced above. In directions nearly normal to the film the light is diffracted chiefly from the wave fronts regularly transmitted through the film and the contributions to the scattered radiation from the part of the wave-front lying on either side of each boundary should obviously be equal. In more oblique directions the scattering occurs chiefly at the curved interface between the two media and the intensities of the pencils emerging respectively after two refractions and after total reflexion are comparable throughout. Thus there is reason to expect throughout the range in which scattered light can be observed the interferences to be strongly marked.

We shall now calculate the intensities of the two interfering pencils. Let the amplitude of the incident beam be unity. Let the two initial parallel pencils of width dx_1 and dx_2 give rise to the two interfering pencils lying between θ and $\theta + d\theta$. The intensities of the two beams will be proportional to dx_1 and dx_2 .

$$\text{Now} \quad \frac{dx_1}{d\theta} = \frac{a \cos i \, d\theta}{2(d_2 - d_1)}$$

$$; \quad \frac{a}{2} \frac{\cos i \cos r \sin i}{\sin i - r} = P_1$$

$$\text{and} \quad \frac{dx_2}{d\theta} = \frac{a}{2} \sin(i - r) = P_2$$

where a = radius of the semicircular edge

The amplitude of the refracted pencil Λ_1 is given by $\left(\frac{P_1}{R}\right)^{\frac{1}{2}}$ where R is the distance of the point of observation. Similarly the reflected beam Λ_2 is given by $\left(\frac{P_2}{R}\right)^{\frac{1}{2}}$. It will be evident from above that while Λ_1 decreases as θ increases Λ_2 increases. In the case of the refracted beam we have to take into consideration the fact that all the light is not completely refracted but part is also reflected. The correction factor is given by Fresnel's co-efficient of refraction

$$\frac{\sin^2 i \cos^2 r}{\sin^2(i+r)} \text{ and } \frac{\sin^2 i \sin^2 r}{\sin^2(i+r) \cos^2(i+r)}$$

for components polarised respectively in the plane of incidence and at right angles to it. This will modify Λ_1 very slightly at first but becomes appreciable at larger angles. We have also to consider the diffraction effect of the edge at O which will be very large for small obliquities but becomes quite negligible at larger angles. This effect might be considered as that due to another ray superposed on the direct rays. The expression for this will be given by Sommerfeld's expression for the diffracted wave at a semi-infinite screen, i.e., by

$$\frac{1}{4\pi} \sqrt{\frac{\lambda}{R}} \left\{ \frac{1}{\cos \frac{\phi+\phi'}{2}} - \frac{1}{\cos \frac{\phi+\phi'}{2}} \right\} \times \cos \frac{2\pi}{\lambda} \left(r - ut + \frac{\pi}{4} \right)$$

where ϕ and ϕ' are the angles made by the diffracted and incident beams with OX respectively.

The amplitude of this beam Λ_3 is given by

$$\frac{1}{4\pi} \sqrt{\frac{\lambda}{R}} \left\{ \frac{1}{\cos \frac{\theta}{2}} - \frac{1}{\sin \frac{\theta}{2}} \right\} \text{ since } \phi = \frac{3\pi}{2} - \theta$$

and

$$\phi' = \frac{\pi}{2}$$

or by

$$-\frac{1}{2\pi} \sqrt{\frac{\lambda}{R}} \frac{1}{\theta} \quad \text{when } \theta \text{ is small}$$

In calculating the amplitude of the resultant the path difference between this and the reflected beam may be neglected. The path difference between the reflected and the twice refracted beams is given by (1). The resultant intensity is obtained by compounding the three beams. The effect due to A_1 vanishes at moderately large angles.

The curve in the figure has been drawn on the above calculations. The asymptotic expansion

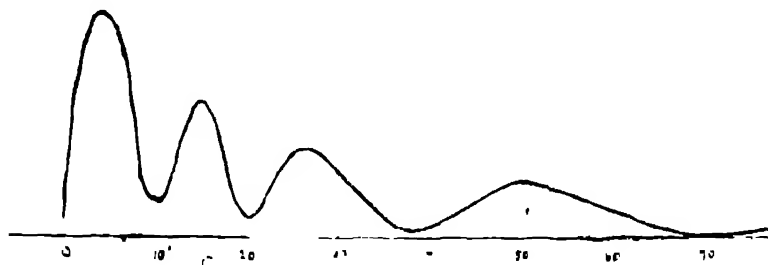


Fig. 2

of A_1 is inapplicable over a small range near 0° and that part of the curve (from 0° to 2°) has been drawn freehand so as to represent as closely as possible the trend of the curve. In the calculation $(\mu-1)t$ has been taken as 5λ .

It will be seen that the general features of the phenomena are well represented by the curve.

We have also to consider the second set of rays LM which are diffracted from the regularly transmitted wave fronts. The amplitudes of both of these will be equal throughout and hence the interferences will be perfect. But as the amplitude diminishes very greatly with moderately large angles its effect will be only seen for small angles. As will be seen from (1) and (2) the two curves will get out of

step at small angles the maximum of one coinciding with the minima of the other, the result being the blurring of the rings which is actually observed.

Position of Achromatic Ring.

The expression for the path-difference of the two interfering pencils given in (1) shows that it diminishes continuously (at first rather rapidly and later more slowly) from $(\mu-1)t$ up to a small fraction of it for the largest angles of diffraction. We have accordingly a series of circular rings in the halo closer together at the centre and wider apart near the margin. The value of δ diminishes gradually from $\frac{\lambda}{2}$ to 0 as θ increases. The outermost ring therefore in white light corresponding to a negligibly small path-difference should be achromatic while the inner ones should be strongly coloured. Near the centre of the halo the colours will not of course be pure. To investigate the exact sequence of colours and to determine whether the achromatisation of the last ring is perfect we have of course to take into account the variation of refractive index μ with wave-length λ . The condition of achromatism is that the path-difference Δ divided by λ should be independent of λ .

The path-difference Δ is given by (1)

$$\Delta = 2\mu a \left\{ \cos i - \sin i \right\} - 2a \cos i - \delta$$

Achromatisation will be perfect when

$$\frac{d}{d\lambda} \left(\frac{\Delta}{\lambda} \right) = 0, \text{ i.e., } \lambda \frac{d\Delta}{d\lambda} = \Delta$$

now

$$\begin{aligned} \frac{d\Delta}{d\lambda} = 2a \left\{ \frac{d\mu}{d\lambda} (\cos i - \sin i) \right. \\ \left. - \left(\mu \cos i - \sin i \right) \frac{dr}{d\lambda} \right\} \text{ approximately} \end{aligned}$$

since

$$\frac{dr}{d\lambda} = \frac{d\mu}{d\lambda} \frac{\sin i}{\cos i}$$

$$\frac{d\Delta}{d\lambda} = \frac{2a}{\cos i} \cdot \frac{d\mu}{d\lambda} \left\{ \cos i - \sin 2i \right\}$$

Assuming μ to be given by Cauchy's formula

$$\mu = A + \frac{B}{\lambda^2}, \quad \frac{d\mu}{d\lambda} = -\frac{2B}{\lambda^3}$$

Hence the condition of achromatisation is given by

$$\begin{aligned} \frac{d\mu}{d\lambda} \frac{\lambda}{\cos i} \left\{ \cos i - \sin 2i \right\} \\ = \mu \left\{ \cos i - \sin i \right\} - \cos i \end{aligned}$$

Assuming μ and $\frac{d\mu}{d\lambda}$ to be the same as that for water we find this condition is satisfied when i is about 40° , *i.e.*, when θ is about 90° . We thus find that the achromatism of the last ring is nearly perfect

Dry Films.

The phenomena exhibited by dry or partially dry films have been described in detail in the first paper of the series. Briefly described it consists of a halo which is much *fainter* than in the case of fresh films showing a broad central area which is achromatic followed *outside* by rings of gradually decreasing width which are strongly coloured. The diffraction halo in fact is very similar to the wellknown diffusion rings observed around the focus of a thick concave mirror with a dusted surface. The resemblance also extends to the case in which the plate is held obliquely in front of the eye. As the plate is inclined, the centre of the halo moves to one side, fresh fringes appearing on that side, and ultimately, as the

plate is held at a moderate obliquity, the halo consists of only arcs of circles, the arc passing through the source being achromatic, the rest being coloured in white light. The explanation of this becomes clear when we understand how drying affects the film. As has been already described, the bubbles of air in the film which are at first lying indiscriminately are drawn together leaving the albumen confined to a number of very fine ridges, the form of these ridges being that of irregular hexagons. In the dry film it is these ridges that form the diffracting centres. The case then becomes similar to diffraction by small particles on the surface of a mirror. If



Fig. 3

A and B be the two diffracting particles and if ϕ be the angle which the direction of the incident light makes with AB and ψ the angle of diffraction it can be easily shown that the positions of maxima and minima are given by

$$l(\cos \phi - \cos \psi) = m \frac{\lambda}{2}$$

or for small angles

$$\psi^2 - \phi^2 = \frac{m\lambda}{l}$$

odd values of m , 1, 3, etc., giving the minima

To test these conclusions the angular diameter of the rings was measured using a monochromatic light source. A small aperture illuminated by a mercury lamp with a green filter forms the source of light. It is viewed through the

film formed between thick flat plates. The angular width of the dark rings in the halo may be determined by making them coincide in succession with a faint luminous reference mark placed in the same plane as the source, the plate being moved in the direction of the incident light. The thickness of the film was determined by observing the spectrum of white light transmitted through the film and noting the wave-lengths of the light freely transmitted through the film without interference.

Results of a few observations are given below.

Thickness of film $t=9\lambda$

Observations in the normal case when $\phi=0$

Number of ring "	Angle ψ (in degree)	$\cos \phi - \cos \psi$ "
	18° 10'	0.050
1	31° 0'	0.048
5	40° 30'	0.048
7	50° 0'	0.051

Observations when $\phi=9^\circ 30'$

Number of ring "	Angle ψ	$\cos \phi - \cos \psi$ "
1	19° 30'	0.045
3	30° 30'	0.042
5	42° 0'	0.048

It is worth while recording another feature exhibited by the dry films. As already described the dry film when held at normal incidence shows a series of circular

rings as shown in the drawing Fig 4(i) When tilted the

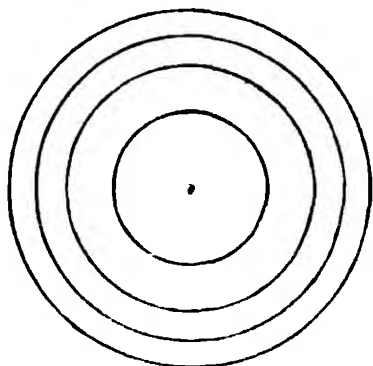


Fig 4(i)

centre of the halo moves to one side fresh fringes appearing on that side, the rings remaining approximately circular as in the case of Newton's rings. When closely examined it is found that when the plate is tilted, besides these circular rings there appear another set of rings cutting the former rings and moving in an opposite direction. At the place where these cut the first set of rings there is present a dislocated appearance. The first set of rings appear displaced at these points, and appear to be slightly bulging at one side. The rings are very faint. Appearance of these rings is shown in the diagram Fig 4(ii). When the plate is very obliquely

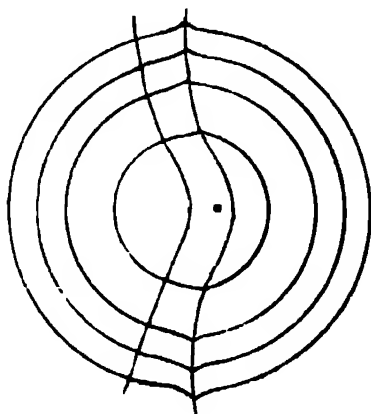


Fig 4 (ii)

held the two sets appear to merge and only arcs of circles are seen as in the case of Newton's diffusion rings. This is shown in Fig 4(ii). The nature of the second set of rings is not yet

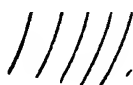


Fig 1(iii)

clear. As already described the film when dry forms into a network of polygonal ridges. It is possible that the peculiar structure of the film may cause the appearance of this second set of rings

Summary.

(1) In this paper the intensity distribution of the halo exhibited by the mixed plate is studied and explained.

(2) The position of the achromatic ring has been determined

(3) The phenomena exhibited by dry films has been shown to belong to the class of Newton's diffusion rings by quantitative measurements

In conclusion the author has much pleasure in recording his best thanks to Prof. C V Raman.

April 1921.

XVII. On the Maintenance of Vibrations under Variable Spring

BY

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INTRODUCTION

Andrew Stephenson¹ was the first to point out that if a body capable of vibration about a position of equilibrium is subject to a periodic force which does not tend directly to displace it from its position of equilibrium but only varies its "spring" or co-efficient of restitution, the force may exercise a cumulative action in intensifying or diminishing the amplitude of the motion, provided the frequency of the force is contained within any one of a number of ranges lying in the vicinity of $1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}$, etc, times the natural frequency of the body. He pointed out that the well-known form of Melde's experiment in which the tension of a string is periodically varied by the action of a force of double its frequency and is set in vibration as a result, is an illustration of the first of the series of the possible types of excitation, a case which had already been discussed by the late Lord Rayleigh. The experimental realisation of the higher types of such maintained vibrations and a general theoretical and qualitative explanation of their distinctive characters was given by C. V. Raman in a well-known memoir.² The present writer has recently had occasion to consider the analogous case of a wire set in vibration by periodic electrical heating,³

¹ On a class of forced oscillations. Quarterly Journal of Pure and Applied Mathematics, June 1906

² Bulletin No 6, The Indian Association for the Cultivation of Science, Calcutta

³ Physical Review, New Series, Vol VI, No 6

and in connection with the phenomena observed, to consider more fully than has been done hitherto the theory of maintenance of vibrations by forces of double frequency¹. It is proposed in the present paper to extend the method of treatment there employed and to put forward a theory capable of quantitative comparison with experiment.

General Theory

We shall first consider the simple case in which a body is assumed to be capable of vibrations having a definite natural frequency, with damping proportional to the first power of the velocity. The differential equation of its motion when it is subject to an imposed periodic variation of spring takes the form

$$\ddot{y} + ky + (n^2 - 2a \sin 2pt)y = 0$$

in which k and a are supposed to be small. In the cases in which n is nearly equal to the frequencies p , or $3p$, or $5p$, etc., and the body is maintained in periodic vibration, we may assume

$$y = A_1 \sin pt + A_3 \sin 3pt + A_5 \sin 5pt + A_7 \sin 7pt + \\ + B_1 \cos pt + B_3 \cos 3pt + B_5 \cos 5pt + B_7 \cos 7pt +$$

Substituting in the differential equation and equating to zero the co-efficients of

$$\sin pt, \cos pt, \sin 3pt, \cos 3pt \text{ etc.},$$

we get

$$(n^2 - p^2)A_1 - (kp + a)B_1 + aB_3 = 0$$

$$(kp - a)A_1 + (n^2 - p^2)B_1 - aA_3 = 0$$

$$-aB_1 + (n^2 - 9p^2)A_3 - 3pkB_3 + aB_5 = 0$$

$$aA_1 + 3pkA_3 + (n^2 - 9p^2)B_3 - aB_5 = 0$$

$$-aB_3 + (n^2 - 25p^2)A_5 - 5pkB_5 + aB_7 = 0$$

$$aA_3 + 5pkA_5 + (n^2 - 25p^2)B_5 - aB_7 = 0$$

and so on.

¹ Phil Mag, Vol XLIV, March 1922,

The product of the *diagonal* elements

$$= \left\{ \left(1 - \frac{n^2}{1^2 p^2} \right) \left(1 - \frac{n^2}{3^2 p^2} \right) \left(1 - \frac{n^2}{5^2 p^2} \right) \left(1 - \frac{n^2}{7^2 p^2} \right) \right\}^{\infty}$$

$$= \cos^2 \frac{n\pi}{2p} \quad \text{since } \cos \theta = \prod_{m=1}^{\infty} \left\{ 1 - \frac{4\theta^2}{(2m-1)^2 \pi^2} \right\}$$

which is absolutely convergent

All the *other* elements in the 3rd and succeeding rows cancel one another and the sum of all the *other* elements in the first two rows is $\frac{2n}{p^2}$. Therefore the sum of all the *other* elements in the infinite determinant is $\frac{2n}{p^2}$ which is also absolutely convergent.

Therefore the infinite determinant is normal and convergent, and it gives the relation between the quantities n , p , a , and k which must be satisfied in order that maintenance may be possible.

Similarly in the cases in which $n=2p$, or $4p$, or $6p$, etc., we may assume

$$\eta = A_1 \sin 2pt + A_2 \sin 4pt + A_3 \sin 6pt +$$

$$+ B_0 + B_1 \cos 2pt + B_2 \cos 4pt + B_3 \cos 6pt +$$

Substituting in the differential equation and equating to zero the sum of the constants and the sum of the co-efficients of $\sin 2pt$, $\cos 2pt$, $\sin 4pt$, $\cos 4pt$, etc., separately, we obtain

$$\begin{aligned} n^2 B_0 - a A_1 &= 0 \\ -2a B_0 + A_1 (n^2 - 4p^2) - 2pk B_2 + a B_4 &= 0 \\ 2pk A_1 + (n^2 - 4p^2) B_3 - a A_5 &= 0 \\ -a B_1 + (n^2 - 16p^2) A_2 - 4pk B_4 + a B_6 &= 0 \\ a A_2 + 4pk A_4 + (n^2 - 16p^2) B_5 - a A_8 &= 0 \\ -a B_2 + (n^2 - 36p^2) A_3 - 6pk B_6 + a B_8 &= 0 \\ n A_3 + 6pk A_6 + (n^2 - 36p^2) B_7 - a A_9 &= 0 \end{aligned}$$

Dividing the first equation by $2\rho^2$, the second and the third by $4\rho^2$, fourth and fifth by $16\rho^2$, sixth and seventh by $36\rho^2$ and changing the signs of all equations except the first, we have

$$\begin{aligned} \frac{n^2}{2\rho^2} B_0 - \frac{n}{2\rho^2} A_1 &= 0 \\ \frac{2n}{2\rho^2} B_0 + \left(1 - \frac{n^2}{2\rho^2}\right) A_1 + \frac{2\rho k}{2\rho^2} B_1 - \frac{n}{2\rho^2} B_1 &= 0 \\ -\frac{2\rho k}{2\rho^2} A_1 + \left(1 - \frac{n^2}{2\rho^2}\right) B_1 + \frac{n}{2\rho^2} A_1 &= 0 \\ \frac{n}{4\rho^2} B_1 + \left(1 - \frac{n^2}{4\rho^2}\right) A_1 + \frac{4\rho k}{4\rho^2} B_1 - \frac{n}{4\rho^2} B_1 &= 0 \\ -\frac{n}{4\rho^2} A_1 - \frac{4\rho k}{4\rho^2} A_1 + \left(1 - \frac{n^2}{4\rho^2}\right) B_1 + \frac{n}{4\rho^2} A_1 &= 0 \\ \frac{n}{6\rho^2} B_1 + \left(1 - \frac{n^2}{6\rho^2}\right) A_1 + \frac{6\rho k}{6\rho^2} B_1 - \frac{n}{6\rho^2} B_1 &= 0 \\ -\frac{n}{6\rho^2} A_1 - \frac{6\rho k}{6\rho^2} A_1 + \left(1 - \frac{n^2}{6\rho^2}\right) B_1 + \frac{n}{6\rho^2} A_1 &= 0 \end{aligned}$$

As before, eliminating the A 's and the B 's, we obtain the infinite determinant,

$$\begin{array}{cccccccccc} \frac{n^2}{2\rho^2} & -\frac{n}{2\rho^2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{n}{2\rho^2} & 1 - \frac{n^2}{2\rho^2} & \frac{k}{2\rho} & 0 & -\frac{n}{2\rho^2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{k}{2\rho} & 1 - \frac{n^2}{2\rho^2} & \frac{n}{2\rho} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{n}{4\rho^2} & 1 - \frac{n^2}{4\rho^2} & \frac{k}{4\rho} & 0 & -\frac{n}{4\rho^2} & 0 & 0 & 0 \\ 0 & -\frac{n}{4\rho^2} & 0 & -\frac{k}{4\rho} & 1 - \frac{n^2}{4\rho^2} & \frac{n}{4\rho^2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{n}{6\rho^2} & 1 - \frac{n^2}{6\rho^2} & \frac{k}{6\rho} & 0 & -\frac{n}{6\rho^2} & 0 \\ 0 & 0 & 0 & -\frac{n}{6\rho^2} & 0 & -\frac{k}{6\rho} & 1 - \frac{n^2}{6\rho^2} & \frac{n}{6\rho^2} & 0 & 0 \end{array}$$

The product of the *diagonal* elements

$$\begin{aligned}
 &= \frac{n^4}{2p^4} \left\{ \left(1 - \frac{n^2}{2^2 p^2} \right) \left(1 - \frac{n^2}{4^2 p^2} \right) \left(1 - \frac{n^2}{6^2 p^2} \right) \dots \right\} \\
 &= \frac{n}{\pi p} \frac{\pi n}{2p} \left\{ \left(1 - \frac{\frac{\pi^2 n^2}{2^2 p^2}}{1^2 \pi^2} \right) \left(1 - \frac{\frac{\pi^2 n^2}{2^2 p^2}}{2^2 \pi^2} \right) \left(1 - \frac{\frac{\pi^2 n^2}{2^2 p^2}}{3^2 \pi^2} \right) \dots \right\} \\
 &= \frac{n}{\pi p} \sin^2 \frac{\pi n}{2p}
 \end{aligned}$$

which is absolutely convergent, since

$$\sin \theta = \theta \prod_{m=1}^{\infty} \left\{ 1 - \frac{\theta^2}{m^2 \pi^2} \right\}$$

The sum of all the *other* terms becomes zero since they cancel one another

Hence the infinite determinant is normal and convergent, and it gives the relation between the quantities n , p , α and k which must be satisfied in order that maintenance may be possible

With reference to the foregoing equations, it may be remarked that in the case $n=p$, a first approximation to the results may be obtained by considering only the terms A_1 and B_1 and neglecting A_2 and B_2 , etc. When $n=3p$ the terms A_1, B_1 and A_3, B_3 must at least be taken into account, A_3, B_3 being relatively of larger magnitude. In general when $n=sp$, the terms up to A_s and B_s must at least be taken into account, the higher terms being neglected. The equation obtained by eliminating the A 's and B 's is correspondingly simplified. Since however, only the ratios of the amplitudes A_1, B_1 , etc., are determinable from the equations and not the amplitudes themselves, the theory outlined is not really adequate for a detailed comparison with the facts of observation. The theory is also inadequate as it indicates that steady maintenance is only possible under certain definite conditions whereas in actual practice there is considerable latitude permissible as regards the magnitude and the frequency of the imposed

variation of spring. It is obvious that the theory requires emendation, being too simple to cover the actual facts. Two modifications of the simple equation may be considered. The first modification is to take into account the change in the free period of the vibrating body which occurs with the increased amplitude. The second modification is in the law of damping which may alter with the magnitude of the vibration. C. V. Raman¹ has shown that a term βy^2 introduced in the part of the equation representing tension provides for the variation proved experimentally to occur in free oscillations of sensible amplitude, due to the second order differences in length between the equilibrium position of the wire and the displaced position of the wire. The frictional force is put down as the sum of two terms, one proportional to the velocity and the other proportional to the square of the velocity.

The First Type

The differential equation for the case in which the frequency of the maintained vibration is one-half of the frequency of the variable spring may be written as

$$y + h'y \pm ky^2 + (n^2 - 2a \sin 2pt + \beta y^2)y = 0$$

The sign \pm indicates that the frictional force changes sign with velocity.

Assume

$$y = A_1 \sin pt + B_1 \cos pt + A_3 \sin 3pt + B_3 \cos 3pt \\ + A_5 \sin 5pt + B_5 \cos 5pt +$$

expand the even function $\cos^2 \left(pt + \tan^{-1} \frac{B_1}{A_1} \right)$ by Fourier's theorem into a series of cosines of multiples of $\left(pt + \tan^{-1} \frac{B_1}{A_1} \right)$ between the limits $-\frac{\pi}{2}$ and $\frac{\pi}{2}$, equate the collected co-efficients

¹ "Photographs of Vibration Curves," Phil. Mag., May 1911

of $\sin pt$ and $\cos pt$ separately to zero. If A stands for amplitude of the maintained vibration, it is found ¹ that

$$\left\{ \frac{3}{4} \beta A^2 - (p^2 - n^2) \right\}^2 = n^2 - p^2 \left[k' + \frac{8}{3\pi} p k A \right]^2$$

It follows that A is not symmetrical with respect to $(p^2 - n^2)$, that there is no resonance 'peak,' that the relation between A and $(p^2 - n^2)$ being nearly parabolic, with the increase of $(p^2 - n^2)$ the amplitude increases to a maximum value and then a sudden collapse of maintenance occurs. Experiments described in the author's paper cited above fully verified all these conclusions.

Again according to Lord Rayleigh's theory, the phase of the maintained vibration is constant and independent of the maintained amplitude. It is found ² experimentally to change with the amplitude. If θ be the phase of the maintained vibration, according to the theory given above,

$$\tan \theta = \frac{B_1}{A_1} = \frac{n^2 - p^2 + \frac{1}{4} \beta A^2}{a + p \left[k' + \frac{8}{3\pi} p k A \right]} = \frac{a - p \left[k' + \frac{8}{3\pi} p k A \right]}{(n^2 - p^2) + \frac{3}{4} \beta A^2}$$

$$\tan^2 \theta = \frac{a - p \left[k' + \frac{8}{3\pi} p k A \right]}{a + p \left[k' + \frac{8}{3\pi} p k A \right]}$$

$$\cos 2\theta = \frac{1 - \tan^2 \theta}{1 + \tan^2 \theta} = \frac{p \left[k' + \frac{8}{3\pi} p k A \right]}{a}$$

$$a \cos 2\theta = p k' + \frac{8}{3\pi} p^2 k A$$

¹ Phil Mag, Vol XLIV, March 1922

² C V Raman, Physical Review, December 1912

In the excess tension end, A limits to zero and therefore $a \cos 2\theta$ limits to the value pk' . For maintenance it has been shown that a should be greater than pk' . Hence the lower limit to $\cos 2\theta$ is the proper fraction $\frac{pk'}{a}$. At the collapse end, A limits to the value $\frac{3\pi}{8p^2k}$ ($a - pk'$) and this value of A makes $\cos 2\theta = 1$. $\cos 2\theta$ therefore increases from a fraction to unity and the phase therefore diminishes from the neighbourhood of $\frac{\pi}{4}$ to zero.

The Second Type.

The differential equation for the case in which the maintained vibration has the same frequency as the variable spring may be written as

$$y + k'y + ky'' + (n^2y - 2ay \sin 2pt + \beta y^3) = 0$$

Assume

$$y = Q + P_1 \sin 2pt + P_2 \cos 2pt$$

Then

$$\ddot{y} = 2p\{P_1 \cos 2pt - P_2 \sin 2pt\}$$

$$y = -4p^2\{P_1 \sin 2pt + P_2 \cos 2pt\}$$

$$-2y \sin 2pt = -P_1 - 2Q \sin 2pt - P_2 \sin 4pt + P_1 \cos 4pt$$

$$y^3 = (Q^3 + 3QP_1^2) + (3P_1^3 + 3P_1Q^2 + 3P_1P_2^2) \sin 2pt$$

$$+ 3P_2^3 + 3P_2Q^2 + 3P_2P_1^2 \cos 2pt$$

+ terms involving sines and cosines of $4pt$ and so on.

Let

$$P^2 = P_1^2 + P_2^2$$

Again

$$y = 2pP \cos\left(2pt + \tan^{-1} \frac{P_2}{P_1}\right) = 2pP \cos \chi, \text{ suppose}$$

Then

$$y^2 = 4p^2 P^2 \cos^2 \chi = f(\chi)$$

$$f(\chi) = -\cos^2 \chi \text{ when } \cos \chi \text{ is negative i.e., when } \chi \text{ varies from } -\pi \text{ to } -\frac{\pi}{2}$$

$$f(\chi) = +\cos^2 \chi \text{ when } \cos \chi \text{ is positive i.e., when } \chi \text{ varies from } -\frac{\pi}{2} \text{ to } +\frac{\pi}{2}$$

$$f(\chi) = -\cos^2 \chi \text{ when } \cos \chi \text{ is negative i.e., when } \chi \text{ varies from } +\frac{\pi}{2} \text{ to } +\pi$$

$$\text{Writing } f(\chi) = \frac{1}{2}b_0 + \sum b_1 \cos \chi + \sum a_1 \sin \chi$$

$$b_r = \frac{1}{\pi} \left\{ \int_{-\pi}^{-\frac{\pi}{2}} -\cos^2 \chi \cos r\chi d\chi + \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \cos^2 \chi \cos r\chi d\chi + \int_{\frac{\pi}{2}}^{\pi} -\cos^2 \chi \cos r\chi d\chi \right\}$$

$$a_r = \frac{1}{\pi} \left\{ \int_{-\pi}^{-\frac{\pi}{2}} -\cos^2 \chi \sin r\chi d\chi + \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \cos^2 \chi \sin r\chi d\chi + \int_{\frac{\pi}{2}}^{\pi} -\cos^2 \chi \sin r\chi d\chi \right\}$$

Then

$$b_0 = 0, \quad a_r = 0 \text{ and } b_1 = \frac{8}{3\pi}$$

Therefore

$$\begin{aligned} \pm k\eta^2 &= 4p^2 P^2 k \left\{ \frac{8}{3\pi} \cos \left(2pt + \tan^{-1} \frac{P^2}{P_1} \right) + \right. \\ &= \frac{32}{3\pi} p^2 P k \left\{ P_1 \cos 2pt - P_1 \sin 2pt \right. \end{aligned} \quad \left. \right\}$$

Substituting these values and equating separately to zero, the sums of the constants and the co-efficients of $\sin 2pt$ and $\cos 2pt$,

$$Q\{n^2 + \beta(Q^2 + \frac{1}{2}P^2)\} = aP_1 \quad (1)$$

$$P_1\{n^2 - 4p^2\} + \beta(\frac{1}{4}P^2 + 3Q^2) - 2pP_1 \left(k' + \frac{16}{3\pi} p P k \right) = 2aQ \quad (2)$$

$$P_2\{(n^2 - 4p^2) + \beta(\frac{1}{4}P^2 + 3Q^2)\} + 2pP_1 \left(k' + \frac{16}{3\pi} p P k \right) = 0 \quad (3)$$

From (3)

$$\frac{P_1}{P_2} = - \frac{2p \left(k' + \frac{16}{3\pi} p P k \right)}{(n^2 - 4p^2) + \beta(\frac{1}{3}P^2 + 3Q^2)} \quad (4)$$

Multiply (2) by P_1 and (3) by P_2 and add,

$$P^2 \{ (n^2 - 4p^2) + \beta(\frac{1}{3}P^2 + 3Q^2) \} = 2 \frac{1}{2} P_1 Q$$

The right-hand side with the help of (1) becomes equal to

$$2Q^2 (n^2 + \beta Q^2 + \frac{1}{3}\beta P^2)$$

$$\frac{P^2}{Q^2} = \frac{2(n^2 + \beta Q^2 + \frac{1}{3}\beta P^2)}{n^2 - 4p^2 + \beta(\frac{1}{3}P^2 + 3Q^2)}$$

The numerator is nearly equal to $2n^2$. In the denominator n^2 is nearly equal to $4p^2$ and $\beta(\frac{1}{3}P^2 + 3Q^2)$ is small in comparison with n^2 . The denominator is therefore small compared with the numerator and therefore Q^2 is small in comparison with P^2 . Therefore Q^2 may be neglected in comparison with P^2 . Divide (2) by P_1 , substitute for $\frac{P_2}{P_1}$ by (4) and for $\frac{Q}{P_1}$ by (1). Then

$$(n^2 - 4p^2) + \beta(\frac{1}{3}P^2 + 3Q^2) + \frac{4p^2 \left(k' + \frac{16}{3\pi} p P k \right)^2}{(n^2 - 4p^2) + \beta(\frac{1}{3}P^2 + 3Q^2)} = \frac{2a^2}{n^2 + \beta(Q^2 + \frac{1}{3}P^2)}$$

Neglect Q^2 in comparison with P^2 and $\beta(Q^2 + \frac{1}{3}P^2)$ in comparison with n^2 , then

$$(n^2 - 4p^2) + \frac{1}{3}\beta P^2 + \frac{4p^2 \left(k' + \frac{16}{3\pi} p P k \right)^2}{(n^2 - 4p^2) + \frac{1}{3}\beta P^2} = \frac{2a^2}{n^2}$$

$$n^2 \{ (n^2 - 4p^2) + \frac{1}{3}\beta P^2 \}^2 - 2a^2 \{ (n^2 - 4p^2) + \frac{1}{3}\beta P^2 \}$$

$$+ 4p^2 n^2 \left(k' + \frac{16}{3\pi} p P k \right)^2 = 0$$

$$\therefore (n^2 - 4p^2) + \frac{1}{3}\beta P^2 = \frac{a^2 \pm \sqrt{a^4 - 4p^2 n^2 \left(k' + \frac{16}{3\pi} p P k \right)^2}}{n^2}$$

The quantity under the radical sign must be positive and hence

$$P < \frac{3\pi}{16pk} \left(\frac{a^2}{2pn^2} - k' \right)$$

At excess tension where P is small, for maintenance to be possible,

$$a^2 > 4p^2 n^2 k', \text{ i.e., } a^2 > 2pn^2 k'$$

Again when P is small, the quantity with the radical sign

$$\left\{ a^2 - 4p^2 n^2 \left(k' + \frac{16}{3\pi} pPk \right) \right\}^{\frac{1}{2}}$$

is equal to

$$\begin{aligned} \{a^2 - 4p^2 n^2 k'\}^{\frac{1}{2}} &= a^2 \left\{ 1 - \frac{4p^2 n^2 k'}{a^2} \right\}^{\frac{1}{2}} \\ &= a^2 \left\{ 1 - \frac{2p^2 n^2 k'}{a^2} \right\} \text{ since } a^2 > 4p^2 n^2 k' \end{aligned}$$

Therefore

$$(n^2 - 4p^2) + \frac{1}{2}\beta P^2 = \frac{a^2}{n^2} \left\{ 1 \pm \left(\frac{2p^2 n^2 k'}{a^2} \right) \right\} = \frac{2a^2}{n^2} \text{ nearly or } = \frac{2p^2 n^2 k'}{a^2}$$

Since the amplitude of vibration increases with the value of a , the first term is the correct one

Hence the expression for the amplitude is

$$a^2 + \sqrt{a^2 - 4p^2 n^2 \left(k' + \frac{16}{3\pi} pPk \right)} \\ \frac{1}{2}\beta P^2 = (4p^2 - n^2) + \dots$$

As in the first case the amplitude increases with the increase of $(4p^2 - n^2)$ and the relation between them is parabolic. The amplitude increases to a maximum value

$$\frac{3\pi}{16pk} \left(\frac{a^2}{2pn^2} - k' \right),$$

and then there is a collapse of maintenance. Again for maintenance to be possible a should be greater than $n\sqrt{2\rho k'}$. An experimental study by the author of the amplitudes of this type of vibrations of a stretched string, forced by an electric motor-vibrator devised by J. A. Fleming and improved by C. V. Raman,¹ has in a general manner, shown the correctness of the above results. A gradual increase of amplitude with diminution of tension and a sudden collapse of maintenance after a maximum amplitude, were observed but the arrangement was not suitable for quantitative determinations. If θ be the phase of the maintained vibration, $\tan \theta = \frac{P}{P'}$

$$\tan \theta = -\frac{2p\left(k' + \frac{16}{3\pi}\rho Pk'\right)}{(n^2 - 4p^2) + \beta\left(\frac{1}{4}P^2 + 3Q^2\right)}$$

When P is small, $\tan \theta$ becomes equal to

$$-\frac{2\rho k'}{n^2} = -\frac{pn^2 k'}{n^2}$$

which is less than $\frac{1}{2}$ since

$$n^2 > 2pn^2 k'$$

When P has the maximum value,

$$\tan \theta = -\frac{\frac{n^2}{a^2}}{\frac{n^2}{a^2}} = -1$$

$\tan \theta$ therefore changes from a value less than $-\frac{1}{2}$ to -1 as the amplitude increases

The Third Type.

In the time taken by the forcing system to complete two vibrations, the vibrating system does in the first type one

¹ Physical Review, November 1919

vibration, in the second type two vibrations, in the third type three vibrations and so on. The photograph¹ of a string executing the third type of vibration, clearly shows that in addition to the two extreme positions, there are two intermediate resting points of the string, one on each side of its equilibrium position. In the equation of motion

$$y + k'y + ky^2 + (u^2 y - 2uy \sin 2pt + \beta y^3) = 0$$

Assume

$$y = P_1 \sin 3pt + P_2 \cos 3pt + Q_1 \sin pt + Q_2 \cos pt$$

Then

$$y = 3p \{ P_1 \cos 3pt - P_2 \sin 3pt \} + p \{ Q_1 \cos pt - Q_2 \sin pt \}$$

$$y = -9p^2 \{ P_1 \sin 3pt + P_2 \cos 3pt \} - p^2 \{ Q_1 \cos pt + Q_2 \sin pt \}$$

$$-2y \sin 2pt = Q_1 \cos 3pt - Q_2 \sin 3pt - (P_1 + Q_1) \cos pt + (P_2 - Q_2) \sin pt +$$

By Fourier's Series,

$$+ky^2 = \frac{24}{\pi} p^2 P_1 P_2 \cos 3pt - \frac{24}{\pi} p^2 P_1 P_2 \sin 3pt$$

If

$$P^2 = P_1^2 + P_2^2 \text{ and } Q^2 = Q_1^2 + Q_2^2$$

$$\beta y^3 = \beta \{ \frac{1}{4} P_1 P^2 + \frac{1}{4} P_2 Q^2 + \frac{1}{4} Q_1^3 - \frac{1}{4} Q_2 Q_1^2 \} \cos 3pt$$

$$+ \beta \{ \frac{1}{4} P_1 P^2 + \frac{1}{4} P_2 Q^2 - \frac{1}{4} Q_1^3 + \frac{1}{4} Q_2 Q_1^2 \} \sin 3pt$$

$$+ \beta \{ \frac{1}{4} Q_1 P^2 + \frac{1}{4} P_2 (Q_1^2 - Q_2^2) + \frac{1}{4} Q_1 Q_2 P_1 + \frac{1}{4} Q_2 Q_1^2 \} \cos pt$$

$$+ \beta \{ \frac{1}{4} Q_1 P^2 + \frac{1}{4} P_2 (Q_1^2 - Q_2^2) - \frac{1}{4} Q_1 Q_2 P_1 + \frac{1}{4} Q_2 Q_1^2 \} \sin pt$$

¹ Figure 1, Plate VI, of C V Raman's bulletin quoted before

Substitute these values in the equation of motion and equate separately to zero the sum of the co-efficients of

$$\sin pt, \cos pt, \sin 3pt, \text{ and } \cos 3pt$$

From the co-efficients of $\sin pt$ and $\cos pt$, omitting terms involving β multiplied with small quantities,

$$Q_1(n^2 - p^2) - Q_2(a - pk) = -aP,$$

$$Q_2(n^2 - p^2) - Q_1(a - pk) = aP,$$

Squaring and adding,

$$Q^2 \{ (n^2 - p^2)^2 + (a - pk)^2 \} = a^2 P^2$$

$$\frac{Q^2}{P^2} = \frac{a^2}{\{(n^2 - p^2)^2 + (a - pk)^2\}}$$

From the co-efficients of $\sin 3pt$ and $\cos 3pt$, omitting terms involving β multiplied with small quantities,

$$P_1 \{ (n^2 - 9p^2) + \frac{1}{2}\beta P^2 + \frac{1}{2}\beta Q^2 \} - 3pkP_2 = aQ_1$$

$$P_2 \{ (n^2 - 9p^2) + \frac{1}{2}\beta P^2 + \frac{1}{2}\beta Q^2 \} + 3pkP_1 = -aQ_2$$

Squaring and adding,

$$P^2 \{ (n^2 - 9p^2) + \frac{1}{2}\beta P^2 + \frac{1}{2}\beta Q^2 \}^2 + P^2 (9pk)^2 = a^2 Q^2 = \frac{a^2 P^2}{\{(n^2 - p^2)^2 + (a - pk)^2\}}$$

$$\{ (n^2 - 9p^2) + \frac{1}{2}\beta P^2 + \frac{1}{2}\beta Q^2 \}^2 = \frac{a^4}{\{(n^2 - p^2)^2 + (a - pk)^2\}} - 9p^2 k^2$$

$$\begin{aligned} & \frac{1}{4} \left\{ \beta + \frac{2a^2}{(n^2 - p^2) + (a - pk)^2} \right\} P^2 \\ &= (9p^2 - n^2) \pm \frac{a^4 - 9p^2 k^2 [(n^2 - p^2)^2 + (a - pk)^2]}{[(n^2 - p^2)^2 + (a - pk)^2]} \end{aligned}$$

which indicates a parabolic relation between the amplitude and the change in tension Experiments give general confirmation of the result

C. V. Raman in his bulletin cited before, has published photographs and vibration curves of the first eleven types of maintained vibrations of strings under variable spring It will be seen from the foregoing that they form a class of maintained vibrations distinct from the usual forms in that they do not have a resonance 'peak' but have the amplitudes gradually increasing to a maximum beyond which a collapse of maintenance occurs

UNIVERSITY COLLEGE, RANGOON,

The 6th August 1923.

XVIII. Scattering of Light by Smoky Quartz

By

NALINI KANTA SUR.

As has been shown by Strutt,¹ the track of a beam of light, in a piece of colourless transparent quartz, though of exceedingly small intensity can be photographed successfully. This track can also be visualised as shown by Raman,² by using a condensed beam of sunlight, provided the quartz be immersed in a vessel of highly refracting liquid, such as turpentine or toluol, and examined against a dark back ground. But the examination of the scattered light in smoky quartz requires no such immersion, as the intensity of the track is fairly strong. A sample of smoky quartz cut perpendicular to the axis, showed a blue track just in the neighbourhood of the convergent incident cone of sunlight, but the colour changed to a brownish tint further along the path, the beam traversing the crystal being along the axis.

Strutt³ has detected the presence of striking coloured bands, when the line of vision is perpendicular to the axis, due to the rotatory dispersion of the crystal, the incident white light being polarised and along the axis. But the method of observation may be varied as pointed out by Raman,⁴ by using an unpolarised beam transverse to the optic axis, and examining the track along the axis through a nicol. The scattering particles in the turbid medium of the smoky quartz polarise the light, and due to rotatory dispersion, the tint changes periodically as the analysing nicol is rotated, or the thickness of the path traversed is

¹ Proc of the Royal Soc, Series A, Vol 95, p 470

² Nature, No 2707, Vol 108, 1921, p 81

³ Strutt, *loc cit*

⁴ Raman, *loc cit*

changed by displacing the crystal gradually along the line of vision.

A comparison of the intensities of vibration in the scattered light, (a) parallel to the direction of the primary beam (weak image), and (b) perpendicular to the direction of the primary beam (strong image) by means of a double image prism and nicol, showed that the weak image had about 5.7¹ per cent. of the intensity of the strong one, whereas Strutt found it to be 3 per cent. for his sample of smoky quartz. Thus it varies to some extent with the specimen used.

It has been emphasised by Strutt in the paper cited above, that the smoky quartz is an optically turbid medium, the scattering being due to inclusions having no relation to the crystalline structure. The examination of the spectrum of the transmitted light shows very clearly that the transparency diminishes gradually from the red end of the visible spectrum towards the violet region. Hence it has been suggested by Raman² that the transparency in the infra-red region may be due to scattering of light, since the intensity of the scattered beam varies inversely as the fourth power of wave-length, the shorter wave lengths will not be transmitted, and the longer heat rays will be allowed to pass through without any diminution of intensity. Hence if the opacity is wholly due to the scattering, the quantity $\lambda \cdot \log \frac{I_0}{I}$, should be constant over the whole range of the spectrum, where I_0 and I are the intensities of the incident and transmitted light, and λ the wave length of the transmitted light. To test this point quantitatively, the absorption co-efficient of the smoky quartz for different wave lengths in the visible region of the spectrum was determined by means of a Nutting photometer and a calibrated spectrometer with a shutter eye piece.

¹ I got this as the mean of six (nearly concordant) readings

² C V Raman, *loc cit.*

For the infra-red region, the comparison between the intensities of the incident and transmitted light was made by an infra-red spectrometer with a linear thermopile supplied by Hilger. The results, due allowance being made for reflection, when plotted show that the absorption coefficient diminishes rapidly but uniformly from the blue towards the red, but in the infra-red the rate of diminution is much smaller. The values of $\lambda \cdot \log \frac{I}{I_0}$, computed for different wave lengths are found to increase at first uniformly from the violet towards the red, and then much more rapidly in the infra red region. Thus we conclude that the opacity of the smoky quartz is not wholly due to scattering, but that there is some genuine absorption also.

That there is some real absorption can also be demonstrated in a different manner. Following Rayleigh,¹ suspensions of sulphur can be obtained by adding a drop of very dilute sulphuric acid to a very weak solution of sodium hyposulphite when the particles are of very small dimensions. Addition of ammonia to arrest the growth dissolves them to some extent, and they were allowed to grow till they reach a steady stage. By trial, a stage can be attained, where the intensity of the scattered light from the sulphur suspension is approximately of the same order as from the smoky quartz, the size of the particles being so small that the scattering from them is effective in the inverse proportion to the fourth power of the wave length. The comparison between the intensities of the scattered light from sulphur-suspensions and the smoky quartz was made by a Rotating Sector Photometer of Hilger, the incident sunlight being concentrated by means of two lenses of equal focal lengths and apertures, so that the original beams were of equal intensity. The absorption co-efficients were determined either by the Nutting photometer or by the sector photometer,

¹ Scientific Papers, Vols. I and IV.

photographic absorption plates of known attenuation coefficient and Wratten colour screen so as to determine it approximately for some definite colour, being used in the latter case

If the absorption is only due to scattering, then $\frac{I_1}{I_2} = \frac{K_1}{K_2}$ where I_1 and I_2 are the intensities of the scattered radiation from quartz and sulphur suspension, and K_1 and K_2 the absorption coefficients respectively. It should be noted that due to the pretty strong absorption of quartz, the intensity of the scattered beam from it depends on the position of the point of incidence of the original beam from the face from which the track is observed. This distance should be noted, and the actual intensity of scattering as unaffected by absorption should be calculated. It was found experimentally that the ratio $\frac{K_1}{K_2}$ is much greater than $\frac{I_1}{I_2}$, thus verifying the previous conclusion.

(I got $\frac{K_1}{K_2} = 42$ nearly and $\frac{I_1}{I_2} = 7$ nearly, the result of two sets of experiments)

The colour of smoky quartz is believed to be due to some form of carbon, and its refractive index for the ordinary ray is 1.560 against 1.544 for the transparent variety as determined by a refractometer. Hence it was of interest to apply the theory developed by Garnett¹ to explain the colour of colloidal solutions of metals, and of coloured glasses containing metal globules. But the existing data² for the extinction coefficient and refractive index of carbon lead to different values for the fraction of volume per unit volume of the smoky quartz occupied by the carbon particles, when calculated from the equations established by Garnett. The ultramicroscopic method of Siedentopf and Szigmondy failed to resolve the particles, and it was not possible to determine directly the number of particles in a given volume. Hence

¹ Phil Trans Roy Soc, Series A, Vol 203, p 385

² See for example H. A. Clark, Phy Rev, Vol 23, No 5,

with the existing data it is not obviously possible to test the validity of the idea, but perhaps there may be some essential similarity between the constitution of smoky quartz and a coloured glass plate having minute metal particles embedded in it

It may be noted that Clark¹ has determined the transmission of very thin cathodic films of carbon, and has found that it decreases almost uniformly from red to $\lambda=226.6 \mu$, beyond which the films are completely opaque. As shown by the authors' measurements the absorption coefficient of the smoky quartz also decreases uniformly from violet to red in the visible region. As the transmission of the cathodic films has not been determined in the infra red, a comparison between the two is not possible in the infra red. But several photographs obtained with a quartz spectrograph with different periods of exposure to the light transmitted through the smoky quartz from an iron arc showed that it was practically opaque beyond 290μ . This may be taken in support of the idea that the colour of the smoky quartz is due to some form of carbon

The experimental work was carried out in the laboratory of the Indian Association for the Cultivation of Science and my best thanks are due to Prof. C. V. Raman for his interest in the work.

¹ H. Senftleben and E. Benedict, *Annalen der Physik*, 1917, Vol 54

XIX. A Study of the Critical Opalescence of Carbon Dioxide.

BY

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Introduction

As is well-known, many substances show a strong and characteristic opalescence near the critical temperature. The phenomenon was studied by Travers and Usher¹ for pure carbon disulphide, sulphur dioxide and ether, by F B Young² for ether, by Keesom³ in a quantitative way for ethylene and very recently by Andant⁴ for ether, methyl, ethyl, butyl and isobutyl acetates. The general theory of the phenomenon for fluids was developed by Einstein⁵ on the basis of the ideas first clearly indicated by Smoluchowski⁶. Einstein's expression for the fraction α of the scattered light is

$$\alpha = (2\pi^2 V/D^2) (RT/N) \frac{\mu^2 (d\mu/dv)^2}{-dp/dv} \lambda^{-1} \sin^2 \psi \quad (1)$$

in which D represents the distance of observation

V the volume of the fluid through which the light passes

ψ the angle between the electric force in the incident light and the direction of observation

and μ is the refractive index

At the critical temperature $-dp/dv=0$. Hence the value α in equation (1) becomes infinity at the critical stage. But

¹ Travers and Usher, Proc Roy Soc A, Vol 78, p 247 (1908)

² F B Young, Phil Mag, Vol 20, p 793 (1910)

³ Keesom, Ann der Physik (1911)

⁴ Andant, Comptes Rendus, 174, May 22 and June 12, 1922

⁵ Einstein, Ann der Physik, Vol 33 (1910)

⁶ Smoluchowski, Ann der Physik, Vol 25 (1908)

this is contrary to experience. Ornstein and Zernike¹ have pointed out that Einstein's assumption that the density fluctuation in different elementary volumes occur independently of each other does not apply very close to the critical temperature. They take the mutual influences into account and modify the formula for opalescence in the form

$$\alpha = \frac{(2\pi^2 V / l^3) (RT/N) v \mu^2 (d\mu/dv)^2 \lambda^{-4} n^2 \psi}{-(dp/dv) + (4\pi^2 RT / v^2) (1 + \cos \phi) (\epsilon / \mu \lambda)^2} \quad (2)$$

where ϕ represents the angle which the direction of observation makes with the incident beam, v the molecular volume ($v = M/\rho$, molecular weight/density), ϵ the radius of action of a single molecule beyond which its influence is zero. At the critical point itself the fraction reduces to

$$(V/2D^3) \frac{v^2 \mu^2 (d\mu/dv)^2 \sin^2 \psi}{N \epsilon^2 (1 + \cos \phi)} \lambda^{-4} \quad (3)$$

Applying the Lorentz-Mosotti formula

$$\frac{\mu^2 - 1}{\mu^2 + 2} = K \rho$$

where K is a constant and ρ is the density, it can be shown by differentiation

$$(d\mu/dv)^2 = (\mu^2 - 1)^2 (\mu^2 + 2)^2 / 36 \mu^2 v^2 \quad (4)$$

Substituting this value of $(d\mu/dv)^2$ in equation (1)

we have

$$\text{for} \quad \psi = \pi/2$$

$$\phi = \pi/2$$

$$\alpha = (\pi^2 RT \beta / 18 N \lambda^4) (\mu^2 - 1)^2 (\mu^2 + 2)^2 \quad (5)$$

¹ Ornstein and Zernike, *Proc Roy Soc, Amsterdam*, Pt I, Vol 17 (1914)

where β is the compressibility
 R is the gas constant
 T is the absolute temperature
 N is the Avogadro number
 α is the fraction of light scattered per unit volume per unit solid angle and in a direction perpendicular to the incident beam.

Substituting the value of $(d\mu/dv)^2$ given by equation (4) in expression (3) we have

$$\alpha_c = \frac{1}{\tau^2} (\mu^2 - 1)^2 (\mu^2 + 2)^2 \mu^2 / N e^2 \lambda^4 \quad (6)$$

where α_c has the same meaning as α in equation (5) for the critical temperature only

The case of carbon dioxide is of special interest in view of the classical works of Andrews,¹ Amagat,² and Jenkin³ from which very complete data for the density and compressibility of the substance are available and also in view of the recent work of Raman and Ramanathan⁴ who have published an extensive series of measurements of the scattering of light in carbon dioxide in different states and over a range of pressures from 1 to 100 atmospheres and temperatures from 0° to 50°C and demonstrated the validity of Einstein's theory over the entire range. Raman and Ramanathan did not however undertake a study of the scattering in the immediate vicinity of the critical state, as here special precautions are necessary in order to obtain reliable results. The present investigation was undertaken by the writer in order to fill up this gap and thus to complete the study of the scattering of light in this substance.

¹ Andrews Phil. Trans (1869), Part II, p 575.

² Amagat Ann Chem Phys (6) 29, p 52 (1893)

³ Jenkin Proc Roy Soc, A, Vol 98, p 170

⁴ Raman and Ramanathan Proc Roy Soc, A, Vol. 104, 1923,

Experimental Technique

Carbon dioxide under examination was enclosed in a sealed tube thus —

A thick-walled spherical bulb was blown from a capillary tube of rather a wide bore. The bulb was cleaned, dried and exhausted and was filled with dry carbon dioxide while it was in liquid air. CO_2 on entering the bulb condensed and when the requisite quantity of solid CO_2 was collected, the bulb was sealed off leaving about five centimeters of the tube as its stem. On removing from liquid air, CO_2 liquefied under its pressure. The liquid occupied 46 of the total volume of the tube at $27^\circ 45 \text{ C}$ and 47 of its volume at 31°C . The meniscus was visible at $31^\circ 13 \text{ C}$ and it disappeared at $31^\circ 2 \text{ C}$. Observations were made by passing light through the liquid.

In practice to have control over the temperature a thermostat had to be devised the scheme of which is shown in

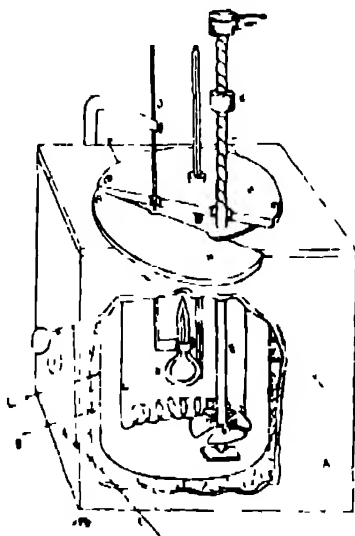
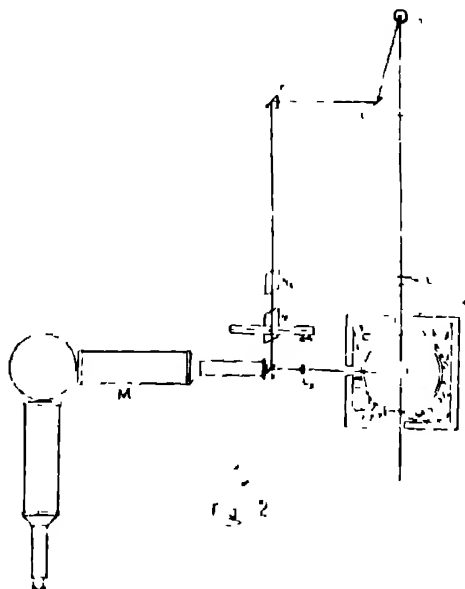


Fig 1

fig. 1, where A is a rectangular box made of wood, B glass wool, C is a coil of german silver wire, L, a glass cylinder, E a stirrer, F a Beckmann Thermometer on which $\frac{1}{100}$ th of a degree Centigrade could be read, J the holder of the observation bulb D and H H the two halves of the lid of the thermostat. G was the shutter of the window which received the light and it was opened or closed as desired by means of the thread *t*. Stirring was done by moving the piece K up and down. Lowering in temperature was done by adding iced water and the rise in temperature was effected by passing a current through the coil C. The temperature of the thermostat could be kept constant by regulating the resistance in series with its heating coil C for any length of time within the range of observation, *i.e.*, 29°C to 35°C.

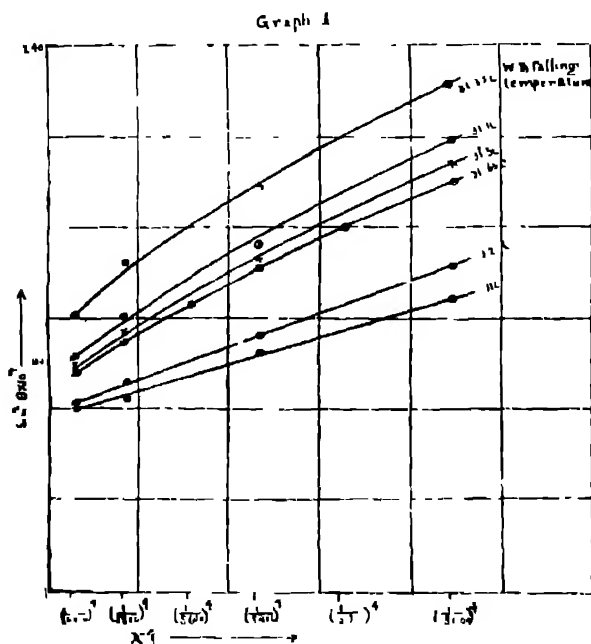


The experimental arrangement is shown in fig. 2 where S is a pointolite lamp of 1,000 candle power, L_1 L_2 are two

achromatic lenses ; P_1 P_2 are two clear Hilger total reflecting prisms , N_1 N_2 are two clear Hilger Nicols , M is a Hilger wavelength spectrometer provided with an ocular slit , P_3 is the prism of the spectrometer ; L_3 is a third lens by which the image of the opalescent track in D is cast on the slit and A is the thermostat containing the observation bulb D . Light from the source S was made parallel by the lens L_1 and the cylinder of rays thus obtained was focussed on the bulb D by means of lens L_2 . A small pencil of rays twice reflected by the prisms P_1 P_2 was allowed to pass through the Nicols N_2 N_1 of which N_1 was provided with a fine graduated circle on which a rotation of one minute could be directly read . The twice reflected direct ray passing through the pair of Nicols N_2 N_1 was made to fall on the spectrometer slit by means of the prism P_3 . To avoid internal reflection, the observation bulb D was placed in a tightly fitting cylinder of black paper having three small apertures of which two were diametrically opposite to each other and the third was on the line perpendicular to that joining the other two . The glass cylinder containing clear distilled water was also painted dead black leaving three patches in positions similar to those on the observation bulb . The observation bulb was so placed in the thermostat that the bundle of rays converged by the lenses L_1 and L_2 could easily pass through it as shown in fig 2. The intensity of the direct beam was controlled by rotating the Nicol N_1 with respect to N_2 . To avoid any change in temperature between the CO_2 inside the bulb and the water surrounding it, the window of the thermostat admitting light was kept closed when readings were not taken . The temperature of the thermostat was kept constant for 15 minutes before a particular observation was made . The spectrum due to the opalescent track became very faint at $29^\circ C$ and $34^\circ C$, so much so, that it was practically impossible to make any comparison with that due to the direct beam in the spectrometer.

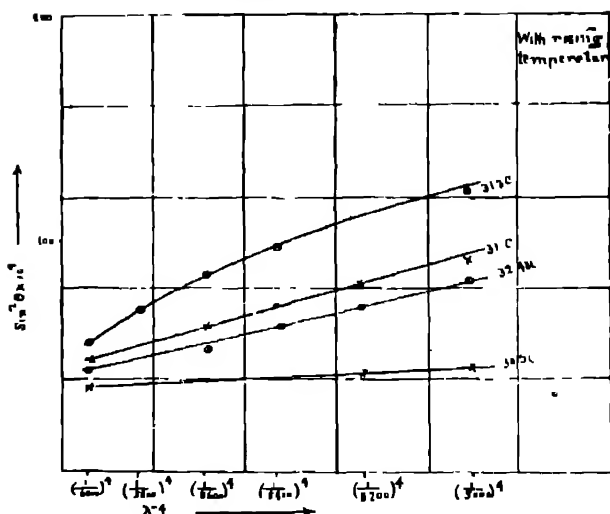
Experimental Results.

Since the two halves of the bands in the spectrometer near any wave-length were made equally intense by turning the Nicol N_1 with respect to N_2 it is easy to see that the intensity of the band was proportional to the square of the sine of its angle of rotation θ . All the values of $\sin^2 \theta$ were plotted against λ^{-4} and some are shown in graphs 1 and 2 where it can be seen that the relationship is represented by straight lines for temperatures lower and higher than the critical point $31^\circ 35 \text{ C}^1$. But the relationship is represented by curved lines immediately in the neighbourhood of $31^\circ 35 \text{ C}$ no matter whether observations were made when the temperature was rising or when the temperature was falling. This clearly shows that for temperatures away from the critical point the law $a = A\lambda^{-4}$ holds and thus supports Einstein's equation (5)



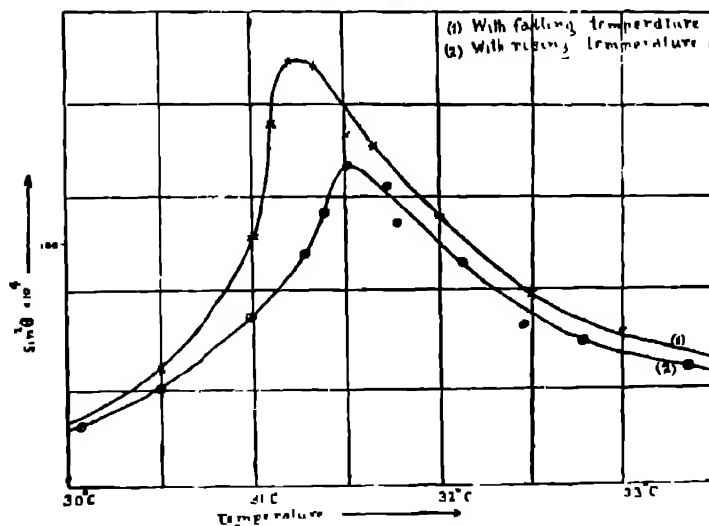
¹ Amagat's value for the critical temperature of CO_2 is $31^\circ 35 \text{ C}$

Graph 2



Graph 3

$$\bar{E}_v \lambda = 5400 \text{ Å}$$



Those values of $\sin^2 \theta$ which when plotted against λ^{-2} gave curved lines were next plotted against λ^{-2} and the relationship was found to be represented by straight lines. This shows that the law $\alpha = B\lambda^{-2}$ also holds in the immediate vicinity of

the critical temperature and this is a clear experimental support of the Ornstein and Zernike equation (3).

Another striking but curious phenomenon observed is represented in graph 3 where it can be seen, as can be seen by comparing graphs 1 and 2, that the intensity for a fixed wave-length with the falling temperature is greater than that with the rising temperature. This phenomenon also attracted the attention of Andant.¹

Absolute Determination of the Intensity of Opalescence.

The arrangement of the apparatus described in fig. 2 was slightly modified in this case. Here (fig 3) a rotating disc Q driven by a motor and the lens L_1 of short focal length were used to alter the intensity as desired.

If R be the total distance (distance of prism P_1 from S + distance between prisms $P_1 P_2$ + distance from prism P_2 from L_2) of L_1 from S , then intensity at $L_1 = Q/4\pi R^2$. Now since the rotating disc obstructs the passage of light intermittently the intensity is reduced to $(1/2\pi) (dl/l) (Q/4\pi R^2)$ where l is the radius of the circle on which the aperture on the disc lies and dl is its width. Considering the apices of the two cones of light meeting at O the focal plane of lens L_2 , the intensity at the spectrometer slit is further diminished to

$$(Q/4\pi R^2) \left(\frac{1}{2\pi} \right) (dl/l) \left\{ 1 \left(\frac{d_2}{d_1} - 1 \right)^2 \right\}$$

where d_1 and d_2 have the meanings as indicated in fig 3

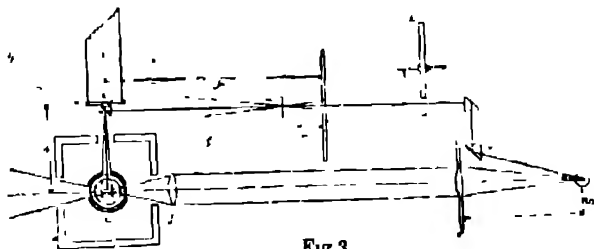


Fig 3

¹ Andant Comptes Rendus, pp 170, June 28, 1920

Again the quantity of light falling on the observation bulb is $Q\pi t^2/4\pi p^2$ or $Qt^2/4p^2$ where t is the radius of the aperture of the lens L_1 and p its distance from the source S . Of this quantity a fraction, say a , is scattered by unit volume of the track per unit solid angle and in a direction at right angles to that of the incident beam.

Therefore the quantity of scattered light falling on the slit of the spectrometer

$$=(Qt^2/4p^2) (a s d\sigma/r^2)$$

where s is the length of the track and r is the distance of the spectrometer slit from the track. But the spectrometer slit of area $d\sigma$ was equally illuminated by the two sources. Hence we have

$$(Qt^2/4p^2) (a s d\sigma/r^2) = dl Q d\sigma 8\pi^2 R^2 l \left(\frac{d_2}{d_1} - 1 \right)^2$$

or

$$a = dl p^2/r^2 \left[\frac{2\pi^2 l s R^2 l^2 \left(\frac{d_2}{d_1} - 1 \right)^2}{d_1^2} \right]$$

In actual experiment

$$\text{Vol. } \lambda = 5400 \text{ \AA}$$

$$\text{temperature} = 30.5^\circ\text{C}$$

$$dl = 1.2 \text{ cms, } l = 10.5 \text{ cms, } P = 42.0 \text{ cms,}$$

$$r = 14.3 \text{ cms, } d_2 = 78.8 \text{ cms, } d_1 = 3.76 \text{ cms,}$$

$$R = 111 \text{ cms, } s = .43 \text{ cm, } t = 1.9 \text{ cms}$$

$$a = \frac{1.2}{2\pi^2} \times \frac{1}{10.5} \times \frac{42^2 \times 14.3^2}{111^2 \times \left(\frac{78.8}{3.76} - 1 \right)^2} \times \frac{1}{43} \times \frac{1}{1.9^2}$$

$$= 2.79 \times 10^{-4}$$

The unknown quantities in equation (5) are $\frac{R}{N}$, β and μ of which $\frac{R}{N}$ is the gas constant¹ and its value is 1.05×10^{-16} . β was found by plotting the reciprocals of the compressibility taken from Jenkin's² work at the saturation points against temperatures up to 23°C. The reciprocal of the compressibility at 31° 35, the critical temperature of CO₂, was considered to be zero. μ^2 was calculated by applying Phillips'³ expressions for CO₂

$$\frac{\mu^2 + 2}{\mu^2 - 1} \rho = 6.581 + 11.3\rho^2$$

where ρ is the density and its value at 30° 5C = 574 (Amagat)

The value of a thus calculated becomes equal to 2.26×10^{-4} . The two results are of the same order and considering the various uncertainties the experimental value agrees fairly well with the calculated one.

The value of a at 30° 5 C being known, a for the critical temperature was calculated from graph 3. From two curves two values of a_c were determined

$$a_c = 9.19 \times 10^{-4} \quad \text{from curve (2)}$$

$$a_c = 10.34 \times 10^{-4} \quad \text{from curve (1)}$$

Taking $a_c = 9.19 \times 10^{-4}$ the value of ϵ becomes 7.9×10^{-7}

With

$$a_c = 10.34 \times 10^{-4}$$

$$\epsilon = 7.5 \times 10^{-7} \text{ cm} \quad (\text{Both b. equation 6})$$

Hence the mean value for $\epsilon = 7.7 \times 10^{-7} \text{ cm}$

¹ Gas constant. Jeans Dynamical Theory of Gases

² Jenkin Proc Roy Soc A, Vol 98, p 170

³ Phillips Proc Roy Soc A, Vol 97, p 225

Thanks are due to Prof C. V Raman for the facilities he gave in conducting the experiment in his own laboratory and for his valuable suggestions.

Summary.

A description of an experiment arranged to study the variation of intensity of opalescence of CO_2 with temperature for wave-lengths ranging from 6000\AA to 5000\AA is given. Results obtained are illustrated in three graphs where it is seen that the law holds for $\alpha = \Lambda\lambda^{-4}$ temperatures away from the critical point, and in the immediate vicinity of the critical temperature the law $\alpha = \Lambda\lambda^{-2}$ holds. It is also seen that the intensity observed with falling temperature is greater than that noted with rising temperature. An arrangement for the absolute determination of intensity of opalescence near any wave-length and at a fixed temperature is also described. The intensity of opalescence at the critical temperature itself is calculated from the experimental data. Finally the value of ϵ , the maximum range of action of a single CO_2 molecule beyond which it has no influence, is calculated and its value is $7.7 \times 10^{-7} \text{ cm}$.

¹ Phillips Proc Roy Soc A, Vol 97, p 235

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